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# THE MEDICAL STUDENT'S

Prof. W. T. Wenzell
San Francisco.

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*of the Publishers,*
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*51 Fifth Avenue,*
*New York.*

W. T. WENZELL,
San Francisco, Cal.

# THE MEDICAL STUDENT'S

# MANUAL OF CHEMISTRY

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BY

R. A. WITTHAUS, A.M., M.D.

Professor of Chemistry, Physics and Toxicology in Cornell University Medical College in New York City; Member of the Chemical Societies of Paris and Berlin; Member of the American Chemical Society; Fellow of the New York Academy of Medicine; of the American Association for the Advancement of Science; of the Medical Society of the State of New York, etc.

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# PREFACE TO THE PRESENT EDITION.

In the edition herewith presented the section on chemical physics has been somewhat extended to include brief consideration of those results of physical investigation which have become most important supports of the principles deduced from observations of chemical phenomena.

The section on mineral chemistry has been condensed to the minimum, and in it the study of the philosophy of chemistry and of the broad principles of the science have been considered, rather than the details of isolated facts or the descriptions of technical processes.

The section on organic chemistry has been rearranged, in great part rewritten, and somewhat extended. The prominence given to this branch of the subject the author believes to be justified, notwithstanding its intricacy and the apparent difficulty of teaching it satisfactorily to medical students, because of the intimate connection of organic chemistry with physiology and with modern pharmacy, and the impossibility of comprehension of the problems of animal and pharmaceutical chemistry without the possession of an adequate knowledge of the principles of organic chemistry.

The references to subjects within the scope of physiological chemistry which were scattered throughout the book in previous editions have been omitted, and the subject has been treated of more in extenso, in its more important branches, in a section by itself, as the importance of this application of chemistry in the medical curriculum undoubtedly demands. This section is devoted to the consideration of the composition of the more important fluids of the body, and of physiological chemical processes; the description of the properties and chemical relationships of substances of physiological interest, which is within the domain of pure chemistry, being contained in the previous sections on mineral and organic chemistry.

The section on laboratory technics, contained in previous editions, has been omitted from this one, as the subjects therein considered are best treated of in a laboratory handbook, which this is not.

The arrangement of the subjects herein considered is that directed

by their logical sequence, but the instructor will probably find it desirable to depart from it somewhat in use. Thus it is suggested that the beginner be taught the properties of a few of the acidulous and basic elements, acids and bases, before being led to the consideration of general principles treated of in the first section.

R. A. W.

NEW YORK, May 1, 1902.

# PREFACE TO THE FIRST EDITION.

In venturing to add another to the already long list of chemical text-books, the author trusts that he may find some apology in this, that the work is intended solely for the use of a class of students whose needs in the study of this science are peculiar.

While the main foundations of chemical science—the philosophy of chemistry—must be taught to and studied by all classes of students alike, the subsequent development of the study in its details must be moulded to suit the purposes to which the student will subsequently put his knowledge. And particularly in the case of medical students, in our present defective methods of medical teaching, should the subject be confined as closely as may be to the general truths of chemistry and its applications to medical science.

In the preparation of this Manual the author has striven to produce a work which should contain as much as possible of those portions of special chemistry which are of direct interest to the medical practitioner, and at the same time to exclude, so far as possible, without detriment to a proper understanding of the subject, those portions which are of purely technological interest. The descriptions of processes of manufactnre are, therefore, made very brief, while chemical physiology and the chemistry of hygiene, therapeutics and toxicology have been dwelt upon.

The work has been divided into three parts. In the first part the principles of chemical science are treated of, as well as so much of chemical physics as is absolutely requisite to a proper understanding of that which follows. A more extended study of physics is purposely avoided, that subject being, in the opinion of the author, rather within the domain of physiology than of chemistry.

The second part treats of special chemistry, and in this certain departures from the methods usually followed in chemical text-books are to be noted. The elements are classed, not in metals and metalloids—a classification as arbitrary as unscientific—but into classes and groups according to their *chemical* characters.

In the text the formula of a substance is used in most instances

in place of its name, *after it has been described*, with a view to giving the student that familiarity with the notation which can only be obtained by continued use.

In the third part those operations and manipulations which will be of utility to the student and physician are briefly described, not with the expectation that these directions can take the place of actual experience in the laboratory, but merely as an outline sketch in aid thereto.

Although the Manual puts forth no claim as a work upon analytical chemistry, we have endeavored to bring that branch of the subject rather into the foreground so far as it is applicable to medical chemistry. The qualitative characters of each element are given under the appropriate heading, and in the third part a systematic scheme for the examination of urinary calculi is given. Quantitative methods of interest to the physician are also described in their appropriate places. In this connection the author would not be understood as saying that the methods recommended are in all instances the best known, but simply that they are the best adapted to the limited facilities of the physician.

The author would have preferred to omit all mention of Troy and Apothecaries' weight, but in deference to the opinions of those venerable practitioners who have survived their student days by half a century, those weights have been introduced in brackets after the Metric, as the value of degrees Fahrenheit have been made to follow those Centigrade.

R. A. W.

BUFFALO, N. Y., September 16, 1883.

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# THE MEDICAL STUDENT'S

# MANUAL OF CHEMISTRY.

## INTRODUCTION.

THE simplest definition of chemistry is a modification of that given by Webster: **That branch of science which treats of the composition of substances, their changes in composition, and the laws governing such changes.**

If a bar of soft iron be heated sufficiently it becomes luminous; if caused to vibrate it emits sound; if introduced within a coil of wire through which a galvanic current is passing, it becomes magnetic and attracts other iron brought near it. Under all these circumstances the iron is still iron, and so soon as the heat, vibration, or galvanic current ceases, it will be found with its original characters unchanged; it has suffered no change in **composition.** If now the iron be heated in an atmosphere of oxygen gas, it burns, and is converted into a substance which, although it contains iron, has neither the appearance nor the properties of that metal. The iron and a part of the oxygen have disappeared, and have been converted into a new substance, differing from either; there has been change in **composition,** there has been **chemical action.** Changes wrought in matter by physical forces, such as light, heat, and electricity, are temporary, and last only so long as the force is active; except in the case of changes in the state of aggregation, as when a substance is pulverized or fashioned into given shape. Changes in chemical composition are permanent, lasting until some other change is brought about by another manifestation of chemical action.

However distinct chemical may thus be from physical forces, it is none the less united with them in that grand correlation whose existence was first announced by Grove, in 1842. As, from chemical action, manifestations of every variety of physical force may be obtained: light, heat, and mechanical force from the oxidation of carbon; and electrical force from the action of zinc upon sulfuric

acid — so does chemical action have its origin, in many instances, in the physical forces. Luminous rays bring about the chemical decomposition of the salts of silver, and the chemical union of chlorin and hydrogen; by electrical action a decomposition of many compounds into their constituents is instituted, while instances are abundant of reactions, combinations, and decompositions which require a certain elevation of temperature for their production. While, therefore, chemistry in the strictest sense of the term, deals only with those actions which are attended by a change of composition in the material acted upon, yet chemical actions are so frequently, nay universally, affected by existing physical conditions, that the chemist is obliged to give his attention to the science of physics, in so far, at least, as it has a bearing upon chemical reactions, to *chemical physics* — a branch of the subject which has afforded very important evidence in support of theoretical views originating from purely chemical reactions.

## PROPERTIES OF MATTER.

**Indestructibility.**—The result of chemical action is change in the composition of the substance acted upon, a change accompanied by corresponding alterations in its properties. Although we may cause matter to assume a variety of different forms, and render it, for the time being, invisible, yet in none of these changes is there the smallest particle of matter destroyed. When carbon is burned in an atmosphere of oxygen, it disappears, and, so far as we can learn by the senses of sight or touch, is lost; but the result of the burning is an invisible gas, whose weight is equal to that of the carbon which has disappeared, plus the weight of the oxygen required to burn it.

**Impenetrability.**—Although one mass of matter may penetrate another, as when a nail is driven into wood, or when salt is dissolved in water, the ultimate particles of which matter is composed cannot penetrate each other, and, in cases like those above cited, the particles of the softer substance are forced aside, or the particles of one substance occupy spaces between the particles of the other. Such spaces exist between the ultimate particles of even the densest substances.

**Weight.**—All bodies attract each other with a force which is in direct proportion to the amount of matter which they contain. The force of this attraction, exerted upon surrounding bodies by the earth, becomes sensible as weight, when the motion of the attracted body toward the center of gravity of the earth is prevented.

In chemical operations we have to deal with three kinds of weight: **absolute, apparent** and **specific.**

**The Absolute Weight** of a body is its weight in vacuo. It is determined by placing the entire weighing apparatus under the receiver of an air-pump.

**The Apparent Weight,** or **Relative Weight,** of a body is that which we usually determine with our balances, and is, if the volume of the body weighed be greater than that of the counter-poising weights, less than its true weight. Every substance in a liquid or gaseous medium suffers a loss of apparent weight equal to that of the volume of the medium so displaced. For this reason the apparent weight of some substances may be a minus quantity. Thus, if the air contained in a vessel suspended from one arm of a poised balance be replaced by hydrogen, that arm of the balance to which the vessel is attached will rise, indicating a diminution in weight.

In stating quantities of any kind the expression must be made in terms of some accepted **unit.** For all measures of extension and weight the unit accepted in all scientific literature is the **metre.**

**The metre** is approximately the 10,000,000th of the quadrant of the earth's meridian, measured from the pole to the equator. It is the distance between two points upon a bar of platinum preserved in the mint at Paris. It is equal to 39.37079 inches.

The metre is subdivided decimally, and its fractions are designated by the Latin numerals. The metre contains 10 **decimetres,** 100 **centimetres,** and 1000 **millimetres** (as the dollar contains 10 dimes, 100 cents, and 1000 mills). The multiples of the metre are designated by the Greek numerals: 10 metres=1 **decametre,** 100 metres =1 **hectometre,** and 1000 metres=1 **kilometre.**

The measures of surface and of volume are expressed in terms of the squares and the cubes of the measures of length. The cubic decimetre is the unit used in measuring liquids and gases, and is called the **litre.** The litre contains 1000 **cubic centimetres** (cc.). It is equal to 1.0567 American quarts, or 0.8802 English quart.

**The gram,** the unit of weight, is a derivative of the metre. It is the absolute weight of a cubic centimetre of distilled water, taken at 4°C.(=39.2° Fahr., the temperature of greatest density of water). The decimal fractions and multiples of the gram are designated in the same manner as are those of the metre. (See Table II, in the appendix.)

**The Specific Weight,** or **Specific Gravity,** of a substance is the weight of a given volume of that substance, as compared with the weight of an equal bulk of some substance, accepted as a standard of comparison, under like conditions of temperature and pressure. The sp. gr. of solids and liquids are referred to water; those of gases to air or to hydrogen.* As, by reason of their different rates

*As the sp. gr. of pure air (hydrogen=1) is 14.42, the sp. gr. in terms of air × 14.42=sp. gr. in terms of hydrogen. Thus, the sp. gr. of hydrochloric acid gas (A=1) is 1.259. Its sp. gr. (H=1) is therefore 1.259 × 14.42=18.155.

of expansion by heat. solids and liquids do not have the same sp. gr. at all temperatures. that at which the observation is made should always be used. or some standard temperature adopted. The standard temperature adopted by some continental writers and in the U. S. P. is 15° 59° F.. Other standard temperatures are 4° 39.2° F.). used by most continental writers. and 15.5° 60° F. . used in Great Britain and to some extent in this country.

In expressing the sp. gr. of heavy liquids the weight of 1 volume of water is taken as unity. Thus the sp. gr. of sulfuric acid being 1.84. 1 cc. of water weighs 1 gram 1 cc. of sulfuric acid weighs 1.84 grams. For the sp. gr. of light liquids 1000 volumes of water are sometimes taken as unity (to avoid numerous fractions . Thus the specific gravity of a urine being 1025. 1000 cc. of the urine will weigh 1025 grams. or 1.025 kilos.

**The relative density** (or. usually. simply **density**) of a substance is the weight of its unit of volume. In metric the specific gravity and density are the same: 1 litre of water weighs 1 kilo. (sp. gr.= 1000), and 1 cc. weighs 1 gram (sp. gr.=1.00). The density of water in terms of the weight of a cubic foot is 62.42 avdp. lbs.. or 75.00 Troy lbs. The word "density" is sometimes used arbitrarily to apply to specific gravity in the aeriform state as referred to hydrogen.

FIG. 1.

To determine the sp. gr. of substances. different methods are adopted, according as the substance is in the solid, liquid, or gaseous state: is in mass or in powder; or is soluble or insoluble in water.

SOLIDS.—*The substance is heavier than water, insoluble in that liquid, and not in powder.*—It is attached by a fine silk fibre or platinum wire to a hook arranged on one arm of the balance, and weighed. A beaker full of pure water is then so placed that the body is immersed in it (Fig. 1), and a second weighing made. By dividing the weight in air by the loss in water, the sp. gr. (water = 1.00) is obtained. Example:

| | |
|---|---|
| A piece of lead weighs in air | 82.0 |
| A piece of lead weighs in water | 74.9 |
| Loss in water | 7.1 |

$$\frac{82.0}{7.1} = 11.55 = \text{sp. gr. of lead}$$

*The substance is in powder, insoluble in water.*—The specific gravity bottle (Fig. 3), filled with water, and the powder, previously

weighed and in a separate vessel, are weighed together. The water is poured out of the bottle, into which the powder is introduced, with enough water to fill the bottle completely. The weight of the bottle and its contents is now determined. The weight of the powder alone, divided by the loss between the first and second weighings, is the specific gravity. Example:

| | |
|---|---|
| Weight of iron filings used | 6.562 |
| Weight of iron filings and sp. gr. bottle filled with water | 148.327 |
| Weight of sp. gr. bottle containing iron filings and filled with water | 147.470 |
| Water displaced by iron | 0.857 |

$$\frac{6.562}{0.857} = 7.65 = \text{sp. gr. of iron.}$$

*The substance is lighter than water.*—A sufficient bulk of some heavy substance, whose sp. gr. is known, is attached to it and the same method followed, the loss of weight of the heavy substance being subtracted from the total loss. Example:

| | |
|---|---|
| A fragment of wood weighs | 4.3946 |
| A fragment of lead weighs | 10.6193 |
| Wood with lead attached weighs in air | 15.0139 |
| Wood with lead attached weighs in water | 5.9295 |
| Loss of weight of combination | 9.0844 |
| Loss of weight of lead in water (determined as above) | 0.7903 |
| Loss of weight of wood | 8.2941 |

$$\frac{4.3946}{8.2941} = 0.529 = \text{sp. gr. of wood}$$

*The substance is soluble in or decomposable by water.*—Its specific gravity, referred to some liquid not capable of acting on it, is determined, using that liquid as water is used in the case of insoluble substances. The sp. gr. so obtained, multiplied by that of the liquid used, is the sp. gr. sought. Example:

| | |
|---|---|
| A piece of potassium weighs | 2.576 |
| A sp. gr. bottle full of naphtha, sp. gr. 0.758, weighs | 22.784 |
| | 25.360 |
| The bottle with potassium and naphtha weighs | 23.103 |
| Loss | 2.257 |

$$\frac{2.576}{2.257} = 1.141 \times 0.758 = 0.865 = \text{sp. gr. of potassium}$$

LIQUIDS.—The sp. gr. of liquids is determined by the **specific gravity balance**, by the **specific gravity bottle**, sometimes called **picnometer**, or by the **spindle or hydrometer.**

*By the balance.*—The liquid, previously brought to the proper temperature, is placed in the cylinder *a* (Fig. 2), and the plunger immersed in it, and attached to the arm of the balance. The weights are now adjusted, beginning with the largest, until the balance is in equilibrium. The sp. gr. indicated by the balance in Fig. 2 is 0.998.

*By the bottle.*—An ordinary analytical balance is used. A bottle of thin glass (Fig. 3), is so made as to contain a given volume of water, say 100 cc., at 15° C., and its weight is determined once for all. To use the *pienometer*, it is filled with the liquid to be examined and weighed. The weight obtained, minus that of the bottle, is

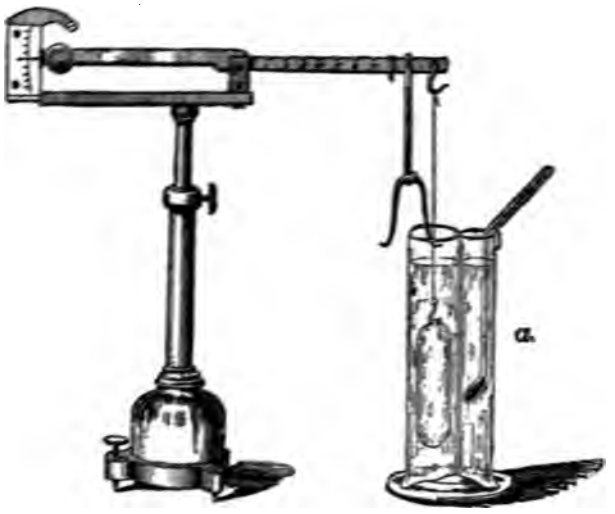



FIG. 2.

the sp. gr. sought, if the bottle contain 1000 c.c.; 1-10 if 100 c.c., etc. Example: Having a bottle whose weight is 35.35, and which contains 100 c.c.; filled with urine it weighs 137.91, the sp. gr. of the urine is $137.91 - 35.35 = 102.56 \times 10 = 1025.6$——Water =1000.

*By the spindle.*—The method by the hydrometer is based upon the fact that a solid will sink in a liquid, whose sp. gr. is greater than its own, until it has displaced a volume of the liquid whose weight is equal to its own: and all forms of hydrometers are simply contrivances to measure the volume of liquid which they displace when immersed. The hydrometer most used by physicians is the urinometer (Fig. 4). It should not be chosen too small, as the larger the bulb, and the thinner and longer the stem, the more accurate are its indications. It should be tested by immersion in liquids of known sp. gr., and the error at different points of the scale should be noted on the

box. The most convenient method of using the instrument is as follows: The cylinder, which should have a foot and rim, but no pouring lip, is filled to within an inch of the top; the spindle is then floated and the cylinder completely filled with the liquid under examination (Fig. 4). The reading is then taken at the highest point *a*, where the surface of the liquid comes in contact with the spindle.*

FIG. 3.

In all determinations of sp. gr. the liquid examined should have the temperature for which the instrument is graduated, as all liquids expand with heat and contract when cooled, and, consequently, the result obtained will be too low if the urine or other liquid be at a temperature above that at which the instrument is intended to be used, and too high if below that temperature. An accurate correction may be made for temperature in simple solutions. In a complex fluid like the urine, however, this can only be done roughly by allowing 1° of sp. gr. for each 3° C. (5.4° F.) of variation in temperature.

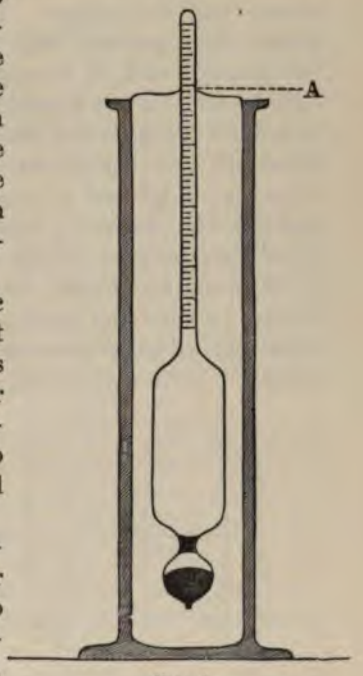



FIG. 4.

GASES AND VAPORS. — The specific gravities of gases and vapors are of great importance in theoretical chemistry, as from them we can determine molecular weights, in obedience to the law of Avogadro (p. 34). The student is referred to works on physics for the methods used for their determination.

**Divisibility.**—All substances are capable of being separated, with greater or less facility, by mechanical means into minute particles. With suitable apparatus, gold may be divided into fragments, visible by the aid of the microscope, whose weight would be $\frac{1}{5000000000000}$ of a grain; and it is probable that when a solid is dissolved in a liquid a still greater subdivision is attained.

* The advantages of the method described over that usually followed are: Greater facility in reading, less liability to error, the possibility of taking the reading in opaque liquids, and the fact that readings are made upward, not downward.

[illegible] no direct experimental evidence of the existence [illegible] divisibility. we are warranted in believing that [illegible] infinitely divisible. A strong argument in favor of [illegible], after physical subdivision has reached the limit [illegible] with regard to compound substances. these may be [illegible] two dissimilar bodies by chemical means.

[illegible] mechanical subdivision is the molecule if the physical [illegible] quantity of matter with which he has to deal. the [illegible] that is capable of free existence.

**States of Matter.**— Matter may exist in one of three "states": [illegible] gas. The term fluid applies to both liquids and gases. [illegible] gases assume the shape and size of the containing [illegible] liquids assume the shape of the containing vessel, but [illegible] definite size. solids are possessed of definite size and

**Crystallization.**— Solid substances exist in two forms, amorphous and crystalline. In the former they assume no geometric [illegible] conduct heat equally well in all directions: they break [illegible] and, if transparent, allow light to pass through them [illegible] in all directions. A solid in the crystalline form has [illegible] geometrical shape: conducts heat more readily in some [illegible] than in others: when broken, separates in certain directions called **planes of cleavage**, more readily than in others: and [illegible] the course of luminous rays passing through it differently when they pass in certain directions than when they pass in others.

**Crystals** are formed in one of four ways: 1. An amorphous substance, by slow and gradual modification, may assume the crystalline form, as vitreous arsenic trioxid (*q. v.*) passes to the crystalline [illegible]. 2. A fused solid, on cooling, crystallizes: as bismuth.

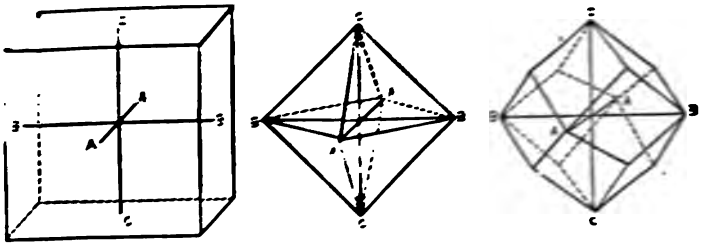


FIG. 5.

3. When a solid is sublimed it is usually condensed in the form of crystals. Such is the case with arsenic trioxid. 4. The usual method of obtaining crystals is by the evaporation of a solution of the substance. If the evaporation be slow and the solution at rest, the crystals are large and well-defined. If the crystals separate by the

sudden cooling of a hot solution, especially if it be agitated during the cooling, they are small.

Most crystals may be divided by imaginary planes into equal, symmetrical halves. Such planes are called **planes of symmetry.**

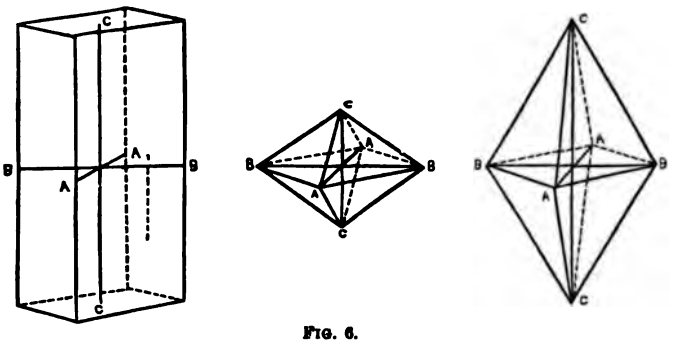



FIG. 6.

Thus in the crystals in Fig. 5 the planes *ab ab*, *ac ac*, and *bc bc* are planes of symmetry.

When a plane of symmetry contains two or more equivalent linear directions passing through the center, it is called the **principal plane of symmetry**; as in Fig. 6 the plane *ab ab*, containing the equal linear directions *aa* and *bb*.

Any normal erected upon a plane of symmetry, and prolonged in both directions until it meets opposite parts of the exterior of the crystal, at equal distances from the plane, is called an **axis of symmetry.**

The axis normal to the principal plane is the **principal axis.** Thus in Fig. 6, *aa*, *bb*, and *cc* are axes of symmetry, and *cc* is the principal axis.

Upon the relations of these imaginary planes and axes a classification of all crystalline forms into six **systems** has been based.

I. **The Cubic, Regular, or Monometric System.**—The crystals of this system have three equal axes, *aa*, *bb*, *cc*, Fig. 5, crossing each other at right angles. The simple forms are the **cube**; and its derivatives, the **octahedron, tetrahedron,** and **rhombic dodecahedron.** The crystals of this system expand equally in all directions when heated, and are not doubly refracting.

II. **The Right Square Prismatic, Pyramidal, Quadratic, Tetragonal, or Dimetric System** contains those crystals having three axes placed at right angles to each other—two as *aa* and *bb*, Fig. 6, being equal to each other and the third, *cc*, either longer or shorter. The simple forms are the **right square prism** and the **right square based octahedron.** The crystals of this system expand equally only in two

**Although we have no direct exp[illegible]** [illegible]ity in all directions. **of a limit to this divisibility, w[illegible]** **matter is not infinitely divisib[illegible]** **system** includes crystals **this view being that, after phys[illegible]** Fig. 7. are of equal **of its power with regard to [illegible]** plane: to which plane **further divided into dissimil[illegible]** the others. is at right

The limit of mechan[illegible] **regular six-sided prism.** the **cist, the smallest quant[illegible]** and the **scalenohedron.** **smallest quantity that is [illegible]** [illegible]ections when heated. and

**States of Matter.**– [illegible] axis. but in other directions **solid, liquid or gas.**

(See also p. 19.) [illegible] **or Trimetric System.**—The [illegible] ing vessel: liquids [illegible] in number. all at right angles have [illegible] [illegible]gth. Fig. 6 represents crystals shape. [illegible] and *cc* to be unequal to each other.

Cry[illegible] **rhombic octahedron,** the right ph[illegible]

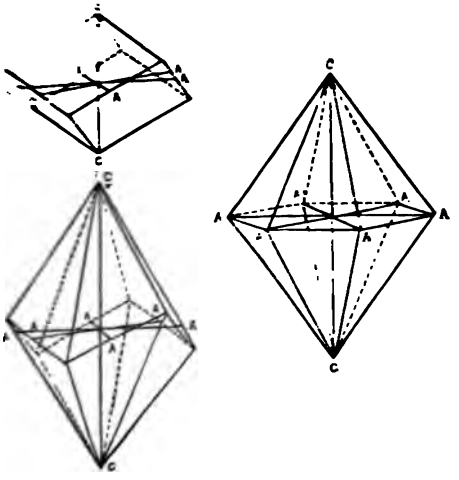


FIG. 7.

[illegible] **prism,** the **right rectangular octahedron,** and the **right rec-** [illegible] **prism.** The crystals of this system, like those of the two [illegible] have no true principal plane or axis.

[illegible] **The Oblique, Monosymmetric, or Monoclinic System.**—The [illegible] of this system have three axes, two of which, *aa*, and *cc*, [illegible] are at right angles; the third, *bb*, is perpendicular to one and [illegible] to the other. They may be equal or all unequal in length. The simple forms are the **oblique rectangular** and **oblique rhombic prism and octahedron.**

VI. **The Doubly Oblique, Asymmetric, Triclinic, or Anorthic** System contains crystals having three axes of unequal length, cross- each other at angles not right angles; Fig. 8, *aa*, *bb*, and *cc* being unequal and the angles between them other than 90°.

The crystals of the fourth, fifth, and sixth systems, when heated, expand equally in the directions of their three axes. They refract light doubly except in two axes.

Secondary Forms.—The crystals occurring in nature or produced artificially have some one of the forms mentioned above, or some modification of those forms. These modifications, or **secondary**

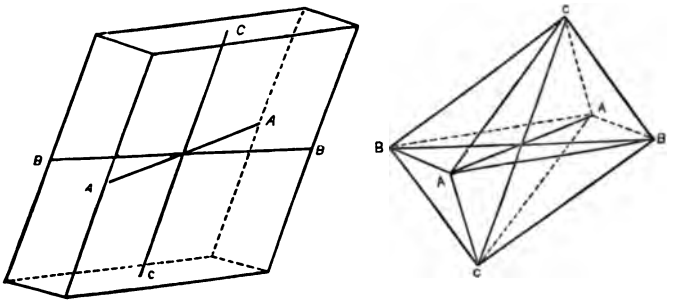



FIG. 8.

**forms**, may be produced by symmetrically removing the angles or edges, or both angles and edges, of the primary forms. Thus, by progressively removing the angles of the cube, the secondary forms shown in Fig. 9 are produced.

It sometimes happens in the formation of a derivative form that alternate faces are excessively developed, producing at length entire obliteration of the others, as shown in Fig. 10. Such crystals are said to be **hemihedral.** They can be developed only in a system having a principal axis.

**Isomorphism.**—In many instances two or more substances crystallize in forms identical with each other, and, in most cases, such substances resemble each other in their chemical constitution. They are said to be **isomorphous.** This identity of crystalline form does not depend so much upon the nature of the elements themselves, as upon the structure of the molecule. The protoxid and peroxid of iron do not crystallize in the same form, nor can they be substituted for each other in reactions without radically altering the properties of the resultant compound. On the other hand, all that class of salts known as alums are isomorphous. Not only are their crystals identical in shape, but a crystal of one alum, placed in a saturated solution of another, grows by regular deposition of the second upon

...sequently added to the crystal, a
...e various salts, layer upon layer.
...substances crystallize, if at all, in
...s modifications, a few bodies are
...ine forms, belonging to different
...morphous. Thus, sulfur, as obtained

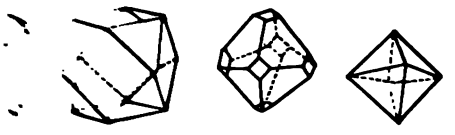


FIG. 9.

...solution in carbon disulfid, forms octahedra,
...system When obtained by cooling melted
...prisms belonging to the fifth system.
...morphism, of the formation of crystals
...systems by the same substance. are also

...assuming the crystalline form, combine with
...ater which exists in the crystal in a solid
...nearly half of the weight of crystallized alum
...called **water of crystallization**, and is nec-
...of the crystalline form, and frequently
...vitriol be heated, it loses its water of crystal-
...converted into an amorphous, white powder. Some
...water of crystallization on mere exposure to the
...said to **effloresce**. Usually, however, they only
...of crystallization when heated (p. 69).
...Dimorphism apart, a few substances are known to
...more than one solid form. These varieties of the same

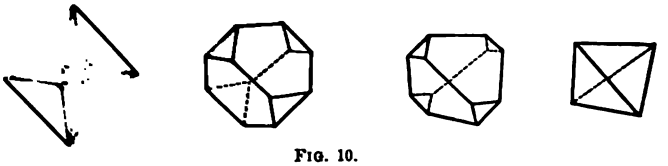


FIG. 10.

substance exhibit different physical properties, while their chemical qualities are the same in kind. Such modifications are said to be **allotropic**. One or more allotropic modifications of a substance are usually crystalline, the other or others amorphous or vitreous. Sulfur, for example, exists not only in two dimorphous varieties of crystals, but also in a third, allotropic form, in which it is flexible

and amorphous. Carbon exists in three allotropic forms: two crystalline, the diamond and graphite; the third amorphous.

In passing from one allotropic modification to another, a substance absorbs or gives out heat.

## PHYSICAL ACTIONS OF CHEMICAL INTEREST.

### HEAT.

**Change of State.**—The state of matter depends upon the heat which it contains and the pressure to which it is subjected. If not chemically decomposed, solids are liquefied, and liquids are vaporized by the application of heat, as when ice is converted into water and into steam by heat. The reverse change, as from steam to ice, is brought about by the abstraction of heat.

The generally accepted theory of heat is that it is caused by an oscillatory or vibratory movement of the molecules of matter, and that this movement is slower or more rapid as the body contains a lesser or greater "amount of heat." Heat tends to overcome cohesion, i. e., the force which unites adjacent molecules; therefore as the rapidity of the molecular movement increases, the cohesion of the molecules of the solid diminishes, until they move freely about each other and the substance is liquid, and, with a still greater rapidity of molecular movement intermolecular attraction is entirely lost, the particles tend to fly apart, and the substance is a gas.

**The effects of heat** upon a body are in doing *internal work:* to raise the temperature of the body, to change its state, or to cause atomic rearrangement, i. e., chemical change; or in doing *external work:* in exerting pressure upon the containing vessel, or in transmitting heat to surrounding bodies.

**Temperature.**—The temperature of a body is the extent to which it can impart sensible heat to surrounding bodies. It is not to be confounded with the *amount* or *quantity of heat* which the body contains. A block of ice just beginning to melt and the same weight of water just beginning to freeze have the same temperature; but heat must be added to the ice to continue its fusion and subtracted from the water to continue its solidification, while during both processes the temperature remains the same in each.

**Thermometers** are instruments for the measurement of temperature. They are usually glass tubes having a bulb blown at one end and closed at the other, the bulb and part of the tube being filled with mercury or with alcohol, whose contraction or expansion indicates a fall or rise of temperature. The alcoholic thermometer is used for measuring low temperatures, and the mercurial for temperatures

between —40° and 360° C. (680° F.). For higher temperatures instruments called pyrometers, based upon the expansion of solids, are used.

In every thermometer there are two *fixed points*, determined by experiment. The lower, or **freezing point**, is fixed by immersing the instrument in melting ice, and marking the level of the mercury in the tube upon the glass when it has become stationary. The higher, or **boiling point**, is similarly fixed by suspending the instrument in the steam from boiling water. The instrument is then graduated according to one of three **scales**: the **Celsius**, or **Centigrade**, the **Fahrenheit**, and the **Réaumur**. The freezing point is marked 0° in the Centigrade and Réaumur scales, and 32° in the Fahrenheit. The boiling point is marked 100° in the Centigrade, 212° in the Fahrenheit, and 80° in the Réaumur scale (Fig. 11). The space between the fixed points is divided into 100 equal **degrees** in the Centigrade scale, into 180° in the Fahrenheit, and in 80° in the Réaumur. Five degrees Centigrade are therefore equal to nine degrees Fahrenheit.

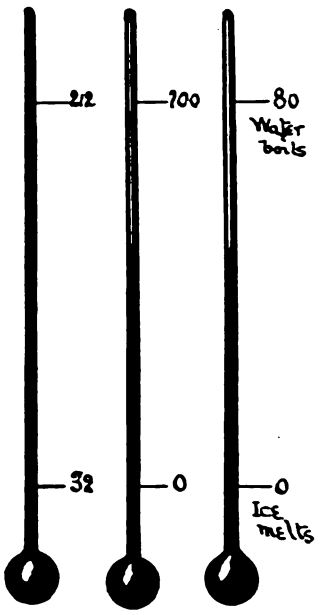


FIG. 11

To convert readings in one scale into terms of another the following formulæ are used:

*Centigrade to Fahrenheit:* Multiply by 9, divide by 5, and add 32. Example: 50° C. × 9 = 450 ÷ 5 = 90 + 32 = 122° = Ans.

*Fahrenheit to Centigrade:* Subtract 32, multiply by 5, and divide by 9. Example: 5° F. — 32 = —27 × 5 = —135 ÷ 9 = —15° = Ans.

**Absolute Temperature.**— As temperature is merely one of the manifestations of heat, and as heat is considered as a mode of motion, the absolute zero of temperature would be reached when the motion causing heat is completely arrested. This temperature is theoretically fixed at —273° C. Therefore —40° C. is 233° on the absolute scale, and 20° C. is 293°.

**Fusion.**—When a solid, not decomposed by heat, is sufficiently heated it **fuses**, or **melts**, becoming a liquid. Bodies which withstand a high degree of heat without fusing are said to be **refractory**.

Every substance begins to melt at a certain temperature, which is invariable for that substance, the pressure remaining constant. This temperature is called the **fusing point** of the substance.

From the moment fusion begins the temperature of the melting body remains constant at the fusing point until fusion is complete, whatever may be the intensity of the heat applied.

The fusing point of a substance is one of the characteristics depended upon for its identification, and frequently as a test for its purity. Some few substances pass by imperceptible stages of gradual softening from the condition of solid to that of liquid, without any fixed fusing point; this is true of iron and glass.

The fusing point is only very slightly influenced by the pressure. That of bodies which contract on fusion is slightly lowered by increase of pressure. In bodies which expand on fusion the fusion point is slightly raised by increase of pressure.

**Latent heat.**—As during the fusion of a solid there is no increase of temperature, notwithstanding that heat is being constantly communicated to the body, the insensible heat so added, which really does work, is said to become **latent.** Each substance has its own latent heat, or **latent heat of fusion,** as it is also called. Thus, if a pound of water at 0°C. be placed in one vessel, and in another similar vessel a pound of ice at 0°C., and the two vessels then immersed in a large vessel of hot water until the ice is melted, the temperature of the melted ice will be found to be 0°C., while the temperature of the water, previously at 0° will be found to be 79.25° C.; therefore the amount of heat which became latent in melting the ice was 79.25°.

**Solution.**—A solid, liquid or gas is said to **dissolve,** or to form a **solution** with a liquid when the two substances unite to form a homogeneous liquid. Solution may be a purely physical process or a physical process attended by a chemical combination.

**In simple or physical solution** there is no modification of the composition of the solvent or of the dissolved substance, and the latter can be reserved, in its primitive form, by simple evaporation of the former. (See p. 29.) During solution, as during fusion of a solid, a certain amount of heat always becomes latent, and consequently physical solution of solids is always attended by diminution of temperature.

**In chemical solution** there is chemical combination between the body dissolved and the solvent, resulting in the formation of a new substance, which then enters into solution. As chemical combinations produce elevation of temperature, the temperature in chemical solution will rise, fall, or remain unchanged according as the increase due to combination is greater or less than the depression due to liquefaction, or the two are equal.

The quantity of solid, liquid, or gas which a liquid can dissolve depends upon the following conditions:

1. *The nature of the solvent and substance to be dissolved.*—The solubility of a substance is one of its distinguishing characteristics, and each substance has a definite solubility in a given liquid. When in speaking of solubility no solvent is mentioned, water is understood to be the solvent referred to.

2. *The temperature* usually has a marked influence on the solubility of a substance. As a rule, water dissolves a greater quantity of a solid substance as the temperature is increased. This increase in solubility is different in the case of different soluble substances. Thus the increase in solubility of the chlorids of barium and of potassium is directly in proportion to the increase of temperature. The solubility of sodium chlorid is almost imperceptibly increased by elevation of temperature. The solubility of sodium sulfate increases rapidly up to 33° (91.4° F.), above which temperature it again diminishes.

The solubility of gases, except hydrogen, in water is the greater the lower the temperature, and the greater the pressure.

The amount of a substance that a given quantity of solvent is capable of dissolving at a given temperature is fixed. A solution containing as much of the dissolved substance as it is capable of dissolving is said to be **saturated**. If made at high temperatures it is said to be a *hot saturated*, and if at ordinary temperatures a *cold saturated solution*.

If a hot saturated solution of a salt be cooled, the solid is in most instances separated by crystallization. If, in the case of certain substances, such as sodium sulfate, however, the solution be allowed to cool while undisturbed no crystallization occurs, and the solution at the lower temperature contains a greater quantity of the solid than it could dissolve at that temperature. Such a solution is said to be **supersaturated**. The contact of particles of solid material with the surface of a supersaturated solution induces immediate crystallization, attended with elevation of temperature.

3. *The presence of other substances already dissolved.*—If to a saturated solution of potassium nitrate, sodium chlorid be added, a further quantity of potassium nitrate may be dissolved. In this case there is double decomposition between the two salts, and the solution contains, besides them, potassium chlorid and sodium nitrate.

4. *The presence of a second solvent.*—If two solvents, *a* and *b*, incapable of mixing with each other, be brought in contact with a substance which both are capable of dissolving; neither *a* nor *b* takes up the whole of the substance to the exclusion of the other, however greatly the solvent power or bulk of the one may exceed that of the other. The relative quantities taken up by each solvent are in a constant ratio.

**Solidification** or **congelation** is the passage of a substance from the liquid to the solid state. It takes place at a fixed temperature, which is the same as that of fusion, and which also remains constant until solidification is complete. The temperature of solidification is called the **freezing point.**

The freezing point of a liquid holding a solid in solution is lower than that of the pure solvent. The amount of lowering of the freezing point is proportionate to the quantity of the solid dissolved; and varies with equal quantities of different substances. (See p. 223.)

When two or more solids, having no chemical action upon each other, are dissolved in a given weight of water the freezing point is lowered by an amount equal to the sum of the depressions that would be caused by each separately. When the observed depression in any case is not in accordance with the statement just made it is evidence that chemical action has taken place between the two substances.

**Law of Raoult.**— If the amount by which the freezing point of a solution containing a fixed quantity of a substance (1 gm. in 100 cc.) is lowered (D) be multiplied by the molecular weight (p. 38) of that substance a constant quantity is obtained. This constant, which is called the **coefficient of molecular depression,** and is represented by the symbol T, is 19 for water, 39 for glacial acetic acid, and 49 for benzene. This law is very serviceable for determining the molecular weights of substances which cannot be volatilized without decomposition (p. 223). Aqueous solutions of acids, bases and salts (p. 42) do not obey the law of Raoult (p. 29).

**Vaporization.**—The passage of a liquid to the gaseous form may take place from the surface of the liquid only, when the process is called **evaporation,** or it may take place throughout the mass of the liquid, when it is called **ebullition,** or **boiling.**

**Volatile liquids** are such as evaporate readily, as alcohol, chloroform, ether. **Fixed liquids** are such as do not evaporate, as the fixed oils and glycerol.

Certain solids, such as iodin, volatilize without passing through the intermediate form of liquid.

Evaporation takes place at all temperatures, although for some substances there is an inferior limit of temperature below which it does not occur. Thus mercury gives off no vapor at temperatures below —10°.

Evaporation is accelerated by (a) increase of temperature; (b) removal of the vapor from the surrounding atmosphere, either by renewal of the atmosphere or by the action of absorbents; (c)

exposure of a large surface of the liquid; (d) diminution of pressure.

**Boiling.**—At a given pressure a liquid begins to boil at a certain temperature, which varies in different liquids, but is always the same in the same liquid. This temperature at 760 mm. of pressure is the **boiling point** of the liquid.

The boiling point remains stationary until the liquid is completely volatilized, whatever the degree of the heat applied.

The boiling point is raised by increase of pressure, and depressed by diminution of pressure.

The boiling point of a liquid holding in solution a substance less volatile than itself is higher than that of the pure solvent. There exists a relation between the molecular weight of the substance dissolved and the degree to which the boiling point is raised similar to the relation between the molecular weight (p. 38) and the depression of the freezing point above referred to (law of Raoult), which is similarly utilized in the determination of molecular weights (p.222).

**Latent heat of vapor.**—The heat required by a liquid to convert it into a vapor, which is insensible as temperature, is the **latent heat of vapor** (p. 15).

A liquid, in evaporating, absorbs heat. It is by this action that the human body is cooled by the evaporation of perspiration from the skin, that local anæsthesia is produced by the evaporation of very volatile liquids, and that cold is produced in refrigerating machines.

**Liquefaction or condensation** is the passage of a gas or vapor to the form of a liquid. It is brought about by chemical action, by cooling, and by compression.

Certain salts, such as calcium chlorid, absorb vapor of water from the air and with it form a solution. They are then said to **deliquesce.**

When vapors are cooled to a temperature below the boiling point of the liquid from which they originated, at the existing pressure, they are condensed.

The process of **distillation** consists in converting a liquid into a vapor by heat and subsequently condensing the vapor by cooling it. Distillation under reduced pressure is frequently resorted to when it is desirable to avoid a temperature as high as the boiling point of the liquid. Fractional distillation is the separation of liquids of different boiling points by distillation and collection of the several fractions separately.

**Sublimation** is a process differing from distillation in that the material acted upon and the product are solid. Sublimation may

or may not be attended by fusion of the original substance. The product is called a **sublimate**, or, if in fine powder, **flowers.**

**Gases and vapors.**—All known gases and vapors have been reduced to the liquid form under the combined influences of cold and pressure.

It has been found that for each gaseous body there exists a certain temperature, above which no amount of pressure will cause its liquefaction, while below that temperature it becomes a liquid under sufficient pressure. This temperature is called the **critical temperature.** For example: the critical temperature of carbon dioxid is 30.9°, and it is liquefied by a pressure of 73 atmospheres at 30°; if the gas at 33° be subjected to a pressure of 100 atmospheres it will remain gaseous until cooled to 30.9°, when it will promptly liquefy.

The **critical pressure** is the pressure at which a gas is liquefied when at the critical temperature.

Aeriform bodies at temperatures above their critical temperatures are sometimes called **true** or **permanent gases**; at temperatures below their critical temperatures they are called **vapors.**

**Thermal Unit.**—The most convenient unit to express quantities of heat is the amount of heat which a given weight of water absorbs or parts with in changing its temperature by a certain amount. The value of this unit is different in different systems: The most generally adopted value is called the **calorie,** and is the amount of heat required to raise 1 kilo. of water through 1 degree Centigrade. The C.G.S. (Centimetre, Gram, Second) value, sometimes called the **small calorie,** is the amount of heat required to raise 1 gram of water through 1 degree Centigrade. In England the unit is similarly based upon the pound and the degree Fahrenheit, and some authors use a compromise value.

**Specific Heat.**—Equal weights of different substances do not possess the same capacity for heat. Thus if equal weights of water and of mercury be exposed to the same source of heat until the water shall have acquired a temperature of 1° C., the mercury will have a temperature of 30°. A given weight of water, therefore, requires 30 times as much heat to raise its temperature through 1° as does an equal weight of mercury, and the capacity for heat of mercury is $\frac{1}{30}$, or 0.0333, that of an equal weight of water.

The specific heat of a substance is the amount of heat required to raise the temperature of one kilo. of that substance through one degree Centigrade, expressed in calories. Thus, the specific heat of mercury is 0.0333, as stated above. The specific heat of a substance is, therefore, its capacity for heat as compared with that of water (p. 37).

OSMOSE—DIFFUSION—DIALYSIS

**Diffusion of Liquids—Dialysis.**—If a liquid be carefully floated upon the surface of a second liquid, of greater density, with which it is capable of mixing, two distinct layers will at first be formed. Even at perfect rest mixture will begin immediately, and progress slowly until the two liquids have **diffused** into each other to form a single liquid whose density is the same throughout.

Substances differ from each other in the rapidity with which they diffuse. Substances capable of crystallization, **crystalloids**, are much more diffusable than those which are incapable of crystallization—**colloids.**

FIG. 12.

If, in place of bringing two solutions in contact with each other, they be separated by a solid or semi-solid, moist, colloid layer, diffusion takes place in the same way through the interposed layer. The phenomenon is then referred to as **osmosis.** Advantage is taken of this fact to separate crystalloids from colloids by the process of **dialysis.** The mixed solutions of crystalloid and colloid are brought into the inner vessel of a **dialyser** (Fig. 12), whose bottom consists of a layer of moist parchment paper, while the outer vessel is filled with pure water. Water passes into the inner vessel, and the crystalloid passes into the water in the outer vessel. By frequently changing the water in the outer vessel, solutions of the proteins or of ferric hydrate, etc., almost entirely free from crystalloids, may be obtained.

**Osmotic pressure.**—It has long been known that in the process of osmosis considerable pressure is exerted upon the walls of the containing vessel. This is designated as the **osmotic pressure.** Recent investigations of the amount and variations of this pressure have shown that it is equal to that which would be exerted by an equal amount of the substance if it were converted into gas, and occupied the same volume, at the same temperature, as the solution. This discovery has afforded another method for the determination of molecular weights, because the osmotic pressure is the same in solutions each containing a different substance in the proportion of its molecular weight. (See p. 222.)

LIGHT.

**The index of refraction** of substances, particularly of oils and aromatic organic liquids, is frequently utilized for their identification, and has furnished data for the determination of their molecular structure. The index of refraction is the ratio between the sine of the angle of incidence and the sine of the angle of refraction: $n = \frac{\text{sin. i}}{\text{sin. r}}$, and is determined with an instrument called a **refractometer**, or with a suitably constructed spectrometer. As the index of refraction varies with the kind of light used, and with the sp.

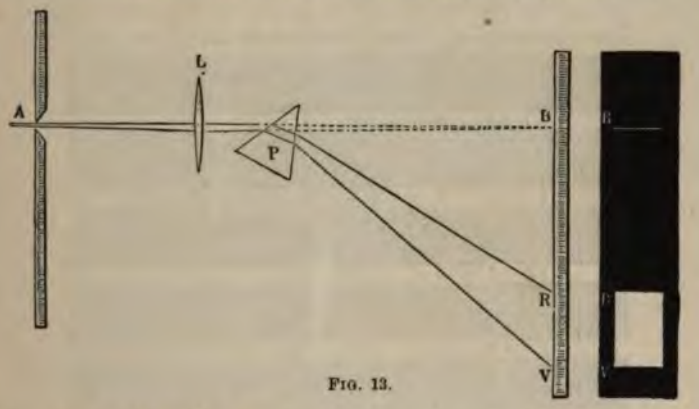



FIG. 13.

gr., therefore with the temperature, yellow (sodium) light is used, and the temperature at which the determination is made is noted in brackets. The symbol $n_D$ is used to indicate the index of refraction for sodium light.

**Spectroscopy.**—A beam of white light, in passing through a prism, is not only **refracted**, or bent into a different course, but is also **dispersed**, or divided into the different colors which constitute the **spectrum** (Fig. 13). The red rays being the least deflected are the **least refrangible**, the violet rays being the most deflected are the **most refrangible.**

A spectrum is of one of three kinds: 1. **Continuous**, consisting of a continuous band of colors: red, orange, yellow, green, blue, cyan-blue, and violet. Such spectra are produced by light from white-hot solids and liquids, from gas-light, candle-light, lime-light, and electric light. 2. **Bright-line spectra**, composed of bright lines upon a dark ground, are produced by glowing vapors and gases. 3. **Absorption spectra** consist of continuous spectra, crossed by dark lines or bands, and are produced by light passing through a solid, liquid, or gas, capable of absorbing certain rays. Examples of bright-line and absorption spectra are shown in Fig. 14, p. 22.

The spectrum of sunlight belongs to the third class. It is not continuous, but is crossed by a great number of dark lines, known as **Fraunhofer's lines,** the most distinct of which are designated by letters (No. 1, Fig. 14).

**The spectroscope** consists of four essential parts: 1st, the slit, *a*, Fig. 15, p. 23; a linear opening between two accurately straight

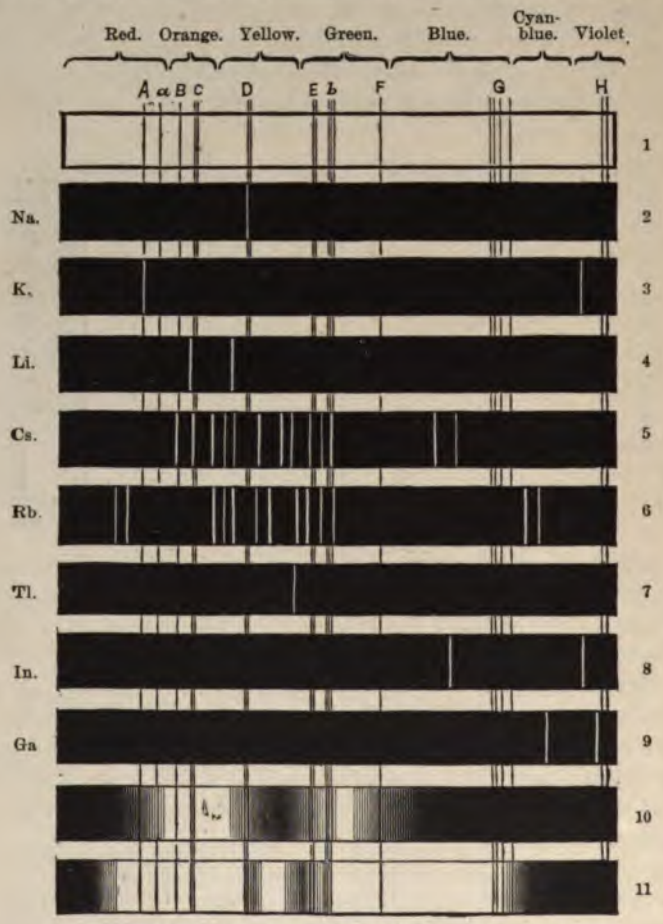



FIG. 14. 1, Solar spectrum; 10 and 11, Absorption spectra.

and parallel knife-edges. 2d, the collimating lens, *b;* a biconvex lens in whose principal focus the slit is placed, and whose object it is to render the rays from the slit parallel before they enter the prism. 3d, the prism, or prisms, *c*, of dense glass, usually of 60°, and so placed that its refracting edge is parallel to the slit. 4th, an observing telescope, *d*, so arranged as to receive the rays as they emerge from

the prisms. Besides these parts spectroscopes are usually fitted with some arbitrary graduation, which serves to fix the location of lines or bands observed.

In direct vision spectroscopes a compound prism is used, so made up of prisms of different kinds of glass that the emerging ray is nearly in the same straight line as the entering ray.

**The micro-spectroscope** (Fig. 16, p. 24) is a direct vision spectroscope used as the eye-piece of a microscope. With it the spectra of very small bodies may be observed.

As the spectra produced by different substances are characterized by the positions of the lines or bands, some means of fixing their location is required. The usual method consists in determining their

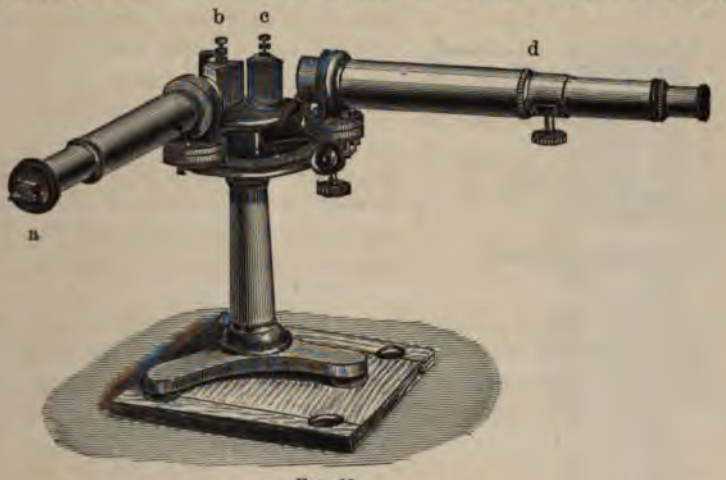



FIG. 15.

relation to the principal Fraunhofer lines. As, however, the relative positions of these lines vary with the nature of the substance of which the prism is made, although their position with regard to the colors of the spectrum is fixed, no two of the arbitrary scales used will give the same reading.

The most satisfactory method of stating the positions of lines and bands is in **wave-lengths.** The lengths of the waves of rays of different degrees of refrangibility have been carefully determined, the unit of measurement being the tenth-metre, of which $10^{10}$ make a metre. The wave-lengths, $=\lambda$, of the principal Fraunhofer lines, are:

| | | | | | |
|---|---|---|---|---|---|
| A | 7604.00 | D | 5892.12 | G | 4307.25 |
| *a* | 7185.00 | E | 5269.13 | $H_1$ | 3968.01 |
| B | 6867.00 | *b* | 5172.00 | $H_2$ | 3933.00 |
| C | 6562.01 | F | 4860.72 | | |

The scale of wave-lengths can easily be used with any spectroscope having an arbitrary scale, with the aid of a curve constructed by interpolation. To construct such a curve, paper is used which is ruled into square inches and tenths. The ordinates are marked with a scale of wave-lengths, and the abscisses with the arbitrary scale of the instrument. The position of each principal Fraunhofer line is then carefully determined in terms of the arbitrary scale, and marked upon the paper with a × at the point where the line of its wave-length and that of its position in the arbitrary scale cross each other. Through these × a curve is then drawn as regularly as possible. In noting the position of an absorption-band, the position of its centre in the arbitrary scale is observed, and its value in wave-lengths obtained from the curve, which, of course, can only be used with the scale and prism for which it has been made. In the Zeiss - Abbé microspectroscope (Fig. 16) a wave-length scale, Fig. 17, p. 25, photographed on glass and placed at N, is used directly. The numbers on the scale are the first two figures of those given above.

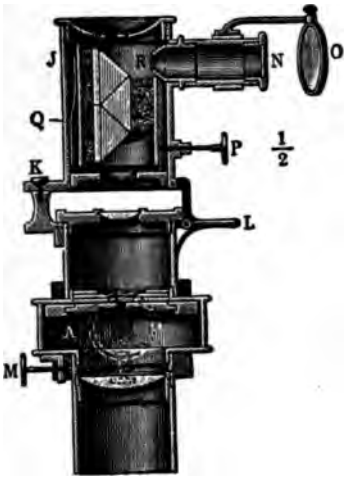


FIG. 16.

**Polarimetry.**—Light, in passing through many crystals in any direction other than parallel to the principal axis (p. 9), is **doubly refracted**, or bifurcated into two rays, the **ordinary** and **extraordinary**, of equal intensity. In then passing through a second, similar crystal, these rays are again bifurcated, forming four rays, which are of equal intensity only in two positions of the second crystal with reference to the first. If the second crystal be rotated about the common axis, two of the rays are gradually extinguished, and, on further rotation, they reappear, and the other two are extinguished. The light in passing through the first crystal has, therefore, been modified in such manner that the second crystal is opaque to the ordinary ray in one position, and to the extraordinary ray in a position opposite to the first. Light so modified is said to be **polarized**, and the first crystal is called the **polarizer**, and the second the **analyzer**. A **Nicol's prism** is a crystal of Iceland spar, so cut that it extinguishes the ordinary ray, transmitting only the extraordinary.

If, when the polarizer and analyzer are so adjusted as to extinguish a ray passing through the former, certain substances are brought between them, light again passes through the analyzer; and

in order again to produce extinction, the analyzer must be rotated upon the axis of the ray to the right or to the left. Substances capable of thus influencing polarized light are said to be **optically active.** If, to produce extinction, the analyzer is turned in the direction of the hands of a watch, the substance is said to be **dextrogyrous;** if in the opposite direction, **lœvogyrous.**

The distance through which the analyzer must be turned depends upon the peculiar power of the optically active substance, the length of the column interposed, the concentration, if in solution, and the wave-length of the original ray of light. The **specific rotary power** of a substance is the rotation produced, in degrees and tenths, by

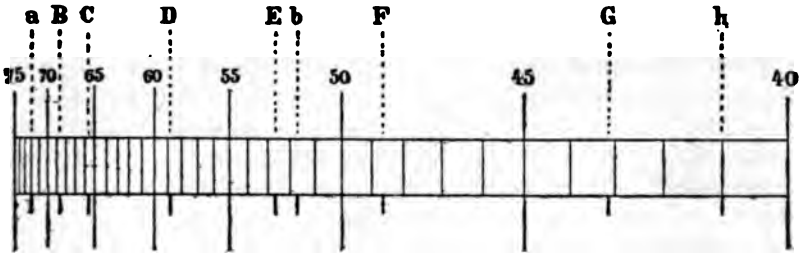



FIG. 17.

one gram of the substance, dissolved in one cubic centimetre of a non-active solvent, and examined in a column one decimetre long. The specific rotary power is determined by dissolving a known weight of the substance in a given volume of solvent, and observing the angle of rotation produced by a column of given length. Then let $p$ = weight in grams of the substance contained in 1 cc. of solution; $l$ the length of the column in decimetres; $a$ the angle of rotation observed; $[a]$ the specific rotary power sought, we have

$$[a] = \frac{a}{pl}.$$

In most instruments monochromatic light, corresponding to the D line of the solar spectrum, is used, and the specific rotary power for that ray is expressed by the sign $[a]_D$. The fact that the rotation is right-handed is expressed by the sign +, and that it is left-handed by the sign —.

It will be seen from the above formula that, knowing the value of $[a]_D$ for any given substance, we can determine the weight of that substance in a solution by the formula

$$p = \frac{a}{[a]_D \times l}.$$

The polarimeter or saccharometer is simply a peculiarly constructed polariscope, used to determine the value of *a*.

**Chemical effects of light.**— Many chemical combinations and decompositions are much modified by the intensity, and the kind of light to which the reacting substances are exposed. Hydrogen and chlorin gases do not combine, at the ordinary temperature, in the absence of light; in diffused daylight or gaslight, they unite slowly and quietly; in direct sunlight, or in the electric light, they unite suddenly and explosively. The salts of silver, used in photography, are not decomposed in the dark, but are rapidly decomposed in the presence of organic matter, when exposed to sunlight.

The chemical activity of the different colored rays of which the solar spectrum is composed is not the same. Those which are the most refrangible possess the greatest chemical activity — the greatest **actinic power.** The visible solar spectrum represents only about one-third of the rays actually emitted from the sun. Two-thirds of the spectrum are invisible as light, and are only recognizable by their heating effects, or by chemical decompositions which they provoke.

## ELECTRICITY.

**Galvanic Electricity.**—If two plates, one of pure zinc, the other of pure copper, be immersed in pure, dilute hydrochloric acid, in such a way that the metals are not in contact with each other, there is no action. But if the two metals be connected, outside of the liquid, by a copper wire, the zinc immediately begins to dissolve, and bubbles of hydrogen gas are collected on, and escape from, the surface of the copper, the action continuing so long as the wire connection is maintained, and ceasing so soon as it is interrupted. If a magnetic compass be approached near to the wire, while it is connected with the two plates, the needle will tend to assume a position at right angles to the wire, whether the latter be in an east and west position or not. But if the wire be disconnected from either plate, the needle returns to its normal, north and south, position. While the two plates are connected by the wire, an **electrical current** is produced by the chemical action between the zinc and hydrochloric acid, and passes through the liquid and through the wire. A similar electrical current is produced whenever two plates which are conductors of electricity are connected with each other by a conducting wire, and the free ends dipped into a liquid which has a more intense chemical action upon one plate than upon the other. Such an arrangement

of plates and liquid is called a **galvanic cell**, and a combination of two or more a **battery.**

The degree of difference between the intensity of the chemical action of the liquid upon the two plates may be likened to the difference in level between two vessels of water connected by a pipe. As the pressure in the water system is the greater the greater the difference in level, so the pressure, or **voltage**, in the electrical system is the greater the greater the difference in potential between two points. As in the water system there is a constant tendency to equalization of pressure by the current flowing toward the lower level, so in the electrical system there is a constant tendency to equalization of potential by the flow of **electrical current** from the higher to the lower potential. The current of electricity differs from that of water, however, in that it is a flow of energy, not a flow of material.

The electrical current therefore originates at that plate having the higher potential (the zinc plate), which is therefore called the **generating, or positive plate.** It flows through the liquid in the cell to the plate of lesser potential (the copper plate), which is therefore called the **collecting, or negative plate.** From the negative plate the current passes through the outside wire toward the generating plate. Any wires or other conductors connected with the plates are called **poles, or electrodes.** As the current leaves the cell from the negative plate, the electrode connected with that plate is of higher potential than that connected with the generating plate, and therefore we have the apparent anomaly that the pole connected with the negative plate is called the **positive pole,** or the **anode,** while the pole connected with the positive plate is called the **negative pole,** or the **cathode.** The entire system of cell, or cells, and outside conductors is called the **circuit.** The circuit is said to be **closed** when the conducting circle is complete. It is **open, or broken,** when it is interrupted at any point.

The difference in potential of an electric generator is referred to as its **electromotive force** (E.M.F.).

Different substances vary greatly in the amount of **resistance** which they offer to the passage of the current through them. Those through which the current passes, with greater or less facility, are called **conductors;** those through which the current will not pass are called **insulators.** The metals are good conductors; vulcanite and mica are insulators.

**The strength of the current** is directly as the E.M.F., and inversely as the resistance, and, consequently, the current strength is the E.M.F. divided by the resistance (Ohm's law).

In electrical measurements the following units are used:

**The ohm** is the unit of resistance. It is the resistance offered by a column of mercury, at 0°C., 106.3 cent. long, weighing 14.4521 gm., and having a uniform cross-section throughout its length.

**The ampère** is the unit of current strength. It is a current which will deposit 4.025 gm. of metallic silver in one hour from a neutral solution of silver nitrate (see electrolysis, below). **A milliampère** is $\frac{1}{1000}$ ampère.

**The volt** is the unit of E.M.F. It is that E.M.F. which, acting steadily through a conductor having a resistance of one ohm will produce a current of one ampère. It is also $\frac{1}{1434}$ the E.M.F. of a standard Clark's cell at 15° C.

**The coulomb** is the unit of electrical quantity. It is the quantity of electricity transferred in one second by a current of one ampère.

**The farad** is the unit of capacity. It is the capacity of a condenser charged to a potential of one volt by one coulomb of electricity.

**The watt** is the unit of energy. It represents the work done by one ampère with a pressure of one volt. One watt per second is equal to $\frac{1}{746}$ of a horse power, or 44.236 foot pounds. The **kilowatt,** 1000 watts, is the unit used by electrical engineers.

**Electrolysis.**—When a galvanic current of sufficient power passes through a liquid compound, or through a solution of a compound, capable of conducting the current, the compound is decomposed. Such decomposition is called **electrolysis,** and the substance so decomposed is known as the **electrolyte.**

When compounds are subjected to electrolysis the constituent elements are not discharged throughout the mass, although the decomposition occurs at all points between the electrodes. In compounds made up of two elements only, one element is given off at each of the poles, entirely unmixed with the other, and, from the same compound, always from the same pole. Thus, if hydrochloric acid be subjected to electrolysis, pure hydrogen is given off at the negative pole and pure chlorin at the positive pole. In this case the hydrogen is said to be **electropositive,** and the chlorin **electronegative.** But if a compound of chlorin and sulfur be electrolysed, the chlorin is given off at the negative pole and the sulfur at the positive. Chlorin is, therefore, electronegative with regard to hydrogen, but electropositive with regard to sulfur.

The results of the electrolysis of binary compounds of the different elements permits of their arrangement in an **electrochemical series,** which is given on opposite page (in the shape of a horseshoe for convenience of printing). In this series each element is electronegative towards all elements between it and the

electropositive end of the list or horseshoe, and electropositive towards all between it and the electronegative end. Arbitrarily, elements electronegative to hydrogen in this series are considered as electronegative elements, those electropositive to hydrogen as electropositive elements.

| ELECTRONEGATIVE. | ELECTROPOSITIVE. |
|---|---|
| Oxygen | Cesium |
| Sulfur | Rubidium |
| Nitrogen | Potassium |
| Fluorin | Sodium |
| Chlorin | Lithium |
| Bromin | Barium |
| Iodin | Strontium |
| Selenium | Calcium |
| Phosphorus | Magnesium |
| Arsenic | Beryllium |
| Chromium | Yttrium |
| Vanadium | Erbium |
| Molybdanum | Aluminum |
| Tungsten | Zirconium |
| Boron | Thorium |
| Carbon | Cerium |
| Antimony | Didymium |
| Tellurium | Lanthanum |
| Tantalum | Manganese |
| Niobium | Zinc |
| Titanium | Iron |
| Silicon | Nickel |
| Hydrogen | Cobalt |
| Gold | Thallium |
| Osmium | Cadmium |
| Iridium | Lead |
| Platinum | Indium |
| Rhodium | Tin |
| Ruthenium | Bismuth |
| Palladium | Uranium |
| Mercury | Copper |
| Silver | |

A similar decomposition takes place with compounds containing more than two elements, one element being liberated at one pole and the remaining group of elements separating at the other. This primary decomposition is generally modified, as to its final products, by subsequent chemical reactions. When, for example, a solution of potassium sulfate is electrolysed, the liquid surrounding the positive electrode becomes acid in reaction (p. 41), and gives off oxygen. At the same time the liquid at the negative side becomes alkaline, and gives off a volume of hydrogen double that of the oxygen liberated. In the first place the potassium sulfate, which consists of potassium, sulfur and oxygen, is decomposed into potassium, which separates at the negative pole; and sulfur and oxygen, combined together, which go to the positive pole. The potassium liberated at the negative pole immediately decomposes the surrounding water, by a secondary action, forming potash, and liberating hydrogen. The sulfur and oxygen group at the positive pole also immediately reacts with water to form sulfuric acid and liberate oxygen.

The primary products of electrolysis, whether consisting of one element only or of groups of elements, are called **ions**. Those which are separated at the negative pole, or cathode, are called **cathions**, those which go to the positive pole, or anode, are called **anions**. The residues of acids (p. 53) are compound ions, that is ions consisting of more than one element.

The phenomena of electrolysis are explained by the supposition, now generally accepted, that aqueous solutions of acids, bases and salts (p. 42) contain, not only those compound substances (p. 31), but also their separated ions in greater or lesser amount, that these ions, by reason of their opposite electrical conditions, are attracted

to the two opposite poles, and that, as they are removed, a further decomposition of the compound into its ions occurs. Thus, in the above examples, the solution of hydrochloric acid contains, not only that substance, but also the ions chlorin and hydrogen; and the solution of potassium sulfate contains the ions potassium and the sulfur-oxygen group. This decomposition of substances in solution into ions is referred to as **ionization**, or as **electrolytic dissociation** (p. 44). The theory of ionization is supported by observed variations in the electrical conductivity of these substances, as well as by their departure from the laws governing variations in freezing and boiling points (p. 17), all of which find their explanations in this hypothesis (see also pp. 44, 45).

The same electrical current decomposes chemically equivalent quantities of all bodies which it traverses (see p. 40).

This fact (Faraday's law) is utilized to calculate the current required to perform a given chemical operation. The weights of elements separated by a given current are to each other as their chemical equivalents; and the quantity of a body decomposed in a given time is proportionate to the strength of the current. Now a current of one ampère, in decomposing water, liberates .000010386 gm. of hydrogen in one second. This is the **electrochemical equivalent** of hydrogen. The electrochemical equivalent of any other element, i. e., the quantity of that element separated by a current of one ampère in one second, is obtained by multiplying .000010386 by the chemical equivalent of that element. For example: taking the chemical equivalent of silver as 107.7; $.000010386 \times 107.7 = .001118$ gm. silver deposited by one ampère of current in 1 sec. $= 4.0248$ gm. in one hour (see Ampère, p. 28).

Electrolytic processes have now replaced older chemical methods of manufacture in many branches of chemical industry, as in the preparation of aluminium, of caustic soda and of bleaching powder.

## CHEMICAL COMBINATION.

**Elements.**—The great majority of the substances existing in and upon the earth may be so decomposed as to yield two or more other substances, distinct in their properties from the substance from whose decomposition they resulted, and from each other. If, for example, sugar be treated with sulfuric acid, it blackens, and a mass of charcoal separates. Upon further examination we find that water has also been produced. From this water we may obtain two gases, differing from each other widely in their properties. Sugar is therefore made up of carbon and the two gases, hydrogen and oxygen; but it has

the properties of sugar, and not those of either of its constituent parts. There is no method known by which carbon, hydrogen and oxygen can be split up, as sugar is, into other dissimilar substances.

**An element is a substance which cannot by any known means be split up into other dissimilar bodies.**

Elements are also called **elementary substances** or **simple substances.**

The number of well-characterized elements at present known is seventy-one.

**Laws governing the combination of elements.**—The alchemists, Arabian and European, contented themselves in accumulating a store of knowledge of isolated phenomena, without, as far as we know, attempting, in any serious way, to group them in such a manner as to learn the laws governing their occurrence. It was not until the latter part of the last century, 1777, that Wenzel, of Dresden, implied, if he did not distinctly enunciate, what is known as the law of reciprocal proportions. A few years later Richter, of Berlin, confirming the work of Wenzel, added to it the law of definite proportions, usually called Dalton's first law. Finally, as the result of his investigations from 1804 to 1808, Dalton added the law of multiple proportions, and reviewing the work of his predecessors, enunciated the results clearly and distinctly.

Considering these laws, not in the order of their discovery, but in that of their natural sequence, we have:

THE LAW OF DEFINITE PROPORTIONS. — **The relative weights of elementary substances in a compound are definite and invariable.** If, for example, we analyze water, we find that it is composed of eight parts by weight of oxygen for each part by weight of hydrogen, and that this proportion exists in every instance, whatever the source of the water. If, instead of decomposing, or **analyzing** water, we start from its elements, and by **synthesis** cause them to unite to form water, we find that, if the mixture be made in the proportion of eight oxygen to one hydrogen by weight, the entire quantity of each gas will be consumed in the formation of water. But if an excess of either have been added to the mixture, that excess will remain after the combination.

**Compounds are substances made up of two or more elements chemically united with each other in definite proportions.** Compounds exhibit properties of their own, which differ from those of the constituent elements to such a degree that the properties of a compound can never be deduced from a knowledge of those of the constituent elements. Common salt, for instance, is composed of 39.32 per cent of the light bluish-white metal,

sodium, and 60.68 per cent of the greenish-yellow, suffocating gas, chlorin.

Compounds made up of two elements only are called **binary** compounds; those consisting of three elements, **ternary** compounds; those containing four elements, **quaternary** compounds, etc.

**A mixture is composed of two or more substances, elements or compounds, mingled in any proportion, without chemical action between the constituents.** The characters of a mixture may be predicated from a knowledge of the properties of its constituents. Thus sugar and water may be mixed in any proportion, and the mixture will have the sweetness of the sugar, and will be liquid or solid, according as the liquid or solid ingredient predominates in quantity.

THE LAW OF MULTIPLE PROPORTIONS.—**When two elements unite with each other to form more than one compound, the resulting compounds contain simple multiple proportions of one element as compared with a constant quantity of the other.**

Oxygen and nitrogen, for example, unite with each other to form five compounds. In these the two elements bear to each other the following relations by weight:

In the first, 14 parts of nitrogen to 8 of oxygen.
In the second, 14 parts of nitrogen to $8 \times 2 = 16$ of oxygen.
In the third, 14 parts of nitrogen to $8 \times 3 = 24$ of oxygen.
In the fourth, 14 parts of nitrogen to $8 \times 4 = 32$ of oxygen.
In the fifth, 14 parts of nitrogen to $8 \times 5 = 40$ of oxygen.

THE LAW OF RECIPROCAL PROPORTIONS.—**The ponderable quantities in which substances unite with the same substance express the relation, or a simple multiple thereof, in which they unite with each other.** Or, as Wenzel stated it, "the weights $b$, $b'$, $b''$ of several bases which neutralize the same weight $a$ of an acid are the same which will neutralize a constant weight $a'$ of another acid; and the weights $a$, $a'$, $a''$ of different acids which neutralize the same weight $b$ of a base are the same which will neutralize a constant weight of another base $b'$." For example: 71 parts of chlorin combine with 40 parts of calcium, and 16 parts of oxygen also combine with 40 parts of calcium, therefore 71 parts of chlorin combine with 16 parts of oxygen, or the two elements combine in the proportion of some simple multiples of 71 and 16.

**The Atomic Theory.**—The laws of Wenzel, Richter, and Dalton, given above, are simply generalized statements of certain groups of facts, and, as such, not only admit of no doubt, but are the foundations upon which chemistry as an exact science is based. Dalton, seeking an explanation of the reason of being of these facts, was led

to adopt the view held by the Greek philosopher, Democritus, that matter was not infinitely divisible. He retained the name *atom* (ἄτομος=indivisible), given by Democritus to the ultimate particles, of which matter was supposed by him to be composed; but rendered the idea more precise by ascribing to these atoms real magnitude, and a definite weight, and by considering elementary substances as made up of atoms of the same kind, and compounds as consisting of atoms of different kinds.

This hypothesis, the first step toward the atomic theory as entertained to-day, afforded a clear explanation of the numerical results stated in the three laws. If hydrogen and oxygen always unite together in the proportion of one of the former to eight of the latter, it is because, said Dalton, the compound consists of an atom of hydrogen, weighing 1, and an atom of oxygen, weighing 8. If, again, in the compounds of nitrogen and oxygen, we have the two elements uniting in the proportion 14:8——14:8×2——14:8×3——14:8×4——14:8×5, it is because they are severally composed of an atom of nitrogen weighing 14, united to 1, 2, 3, 4, or 5 atoms of oxygen, each weighing 8. Further, that compounds do not exist in which any fraction of 8 oxygen enters, because 8 is the weight of the indivisible atom of oxygen.

Dalton's hypothesis of the existence of atoms as definite quantities did not, however, meet with general acceptance. Davy, Wollaston, and others considered the quantities in which Dalton had found the elements to unite with each other, as mere *proportional numbers* or *equivalents*, as they expressed it, nor is it probable that Dalton's views would have received any further recognition at that time had their publication not been closely followed by that of the results of the labors of Humboldt and of Gay Lussac, concerning the *volumes* in which gases unite with each other.

In the form of what are known as Gay Lussac's laws, these results are:

**First.—There exists a simple relation between the volumes of gases which combine with each other.**

**Second.—There exists a simple relation between the sum of the volumes of the constituent gases, and the volume of the gas formed by their union.** For example:

1 volume chlorin unites with 1 volume hydrogen to form 2 volumes hydrochloric acid.
1 volume oxygen unites with 2 volumes hydrogen to form 2 volumes vapor of water.
1 volume nitrogen unites with 3 volumes hydrogen to form 2 volumes ammonia.
1 volume oxygen unites with 1 volume nitrogen to form 2 volumes nitric oxid.
1 volume oxygen unites with 2 volumes nitrogen to form 2 volumes nitrous oxid.

Berzelius, basing his views upon these results of Gay Lussac, modified the hypothesis of Dalton and established a distinction between the *equivalents* and *atoms*. The composition of water he expressed, in the notation which he was then introducing, as being $H_2O$, and not HO as Dalton's hypothesis called for. As, however, Berzelius still considered the atom of oxygen as weighing 8, he was obliged also to consider the atoms of hydrogen and of certain other elements as double atoms — a fatal defect in his system, which led to its overthrow, and to the re-establishment of the formula HO for water.

It was reserved to Gerhardt to clearly establish the distinction between atom and molecule; to observe the bearing of the discoveries of Avogadro and Ampère upon chemical philosophy; and thus to establish the atomic theory as entertained at present.

As a result of his investigations in the domain of organic chemistry, Gerhardt found that, if Dalton's equivalents be adhered to, whenever carbon dioxid or water is liberated by the decomposition of an organic substance, it is invariably in double equivalents, never in single ones. Always $2CO_2$ or 2HO, or some multiple thereof, never $CO_2$ or HO. He further found that if the equivalents $C = 6$, $H = 1$, and $O = 8$ be retained, the formula became such that the equivalents of carbon are always divisible by two. In fact, he found the same objections to apply to the notation then in use that had been urged against that of Berzelius.

In 1811, Avogadro, from purely physical researches, had been enabled to state the law which is now known by his name, to the effect that **equal volumes of all gases, under like conditions of temperature and pressure, contain equal numbers of molecules.**

This law is also known as the law of Ampère, the French physicist having enunciated it about the same time as, and independently of, his Italian colaborer.

In the hands of Gerhardt this law, in connection with those of Gay Lussac, became the foundation of what is sometimes called the "new chemistry." Bearing in mind Avogadro's law, we may translate the first three combinations given in the table on p. 33 into the following:

1 molecule chlorin unites with 1 molecule hydrogen, to form 2 molecules hydrochloric acid.

1 molecule oxygen unites with 2 molecules hydrogen, to form 2 molecules vapor of water.

1 molecule nitrogen unites with 3 molecules hydrogen, to form 2 molecules ammonia.

But the ponderable quantities in which these combinations take place are:

35.5 chlorin to . . . . . 1 hydrogen.
16 oxygen to . . . . . 2 hydrogen.
14 nitrogen to . . . . . 3 hydrogen.

And as single molecules of hydrogen, oxygen and nitrogen are in these combinations subdivided to form 2 molecules of hydrochloric acid, water and ammonia, it follows that these molecules must each contain two equal quantities of hydrogen, oxygen and nitrogen, less in size than the molecules themselves. And, further, as in these instances each molecule contains two of these smaller quantities, or **atoms**, the relation between the weights of the molecules must also be the relation between the weights of the atoms, and we may therefore express the combinations thus:

1 atom chlorin weighing 35.5 unites with one 1 atom hydrogen weighing 1;
1 atom oxygen weighing 16 unites with 2 atoms hydrogen weighing 2;
1 atom nitrogen weighing 14 unites with 3 atoms hydrogen weighing 3;

and consequently, if the atom of hydrogen weighs 1, that of chlorin weighs 35.5, that of oxygen 16, and that of nitrogen 14.

**Atomic Weight.**—The distinction between molecules and atoms may be expressed by the following definitions:

**A molecule is the smallest quantity of any substance that can exist in the free state.**

**An atom is the smallest quantity of an elementary substance that can enter into a chemical reaction.**

The molecule is always made up of atoms, upon whose nature, number and arrangement with regard to each other, the properties of the substance depend. In an elementary substance the atoms composing the molecules are the same in kind, and usually two in number. In compound substances they are dissimilar, and vary in quantity from two in a simple compound, like hydrochloric acid, to hundreds or thousands in more complex substances.

**The word atom can only be used in speaking of an elementary body, and that only while it is passing through a reaction. The term molecule applies indifferently to elements and compounds.**

The atoms have definite relative weights; and upon an exact determination of these weights depend the entire science of quantitative analytical chemistry. (See Stoichiometry, p. 47.) They have been determined by repeated and careful analyses of perfectly pure compounds of the elements, and **express the weight of one atom of the element as compared with the weight of one atom of hydrogen,** that being the lightest element known. It is also the weight of a

volume of the element, in the form of gas, which would occupy the same volume, under like pressure and temperature, as an amount of hydrogen weighing one. What the *absolute weight* of an atom of any element may be we do not know.

The atomic weight of oxygen is 15.87. Some chemists prefer a system of atomic weights in which that of oxygen is 16; when that of hydrogen becomes 1.008. The following table contains a list of the elements at present known, with their atomic weights, calculated with H = 1; and with O = 16.*

ELEMENTS.

| Name. | Symbol. | Valence. | Atomic Weight, H=1. | Atomic Weight, O=16. |
|---|---|---|---|---|
| Aluminium | Al | IV ($Al_2$), vi | 26.88 | 27.1 |
| Antimony | Sb | III, V | 119.04 | 120. |
| Argon | A | ? | 39.68 | 40. |
| Arsenic | As | III, V | 74.4 | 75. |
| Barium | Ba | II | 136.3 | 137.4 |
| Beryllium (Glucinum) | Be | II | 9.02 | 9.1 |
| Bismuth | Bi | III, V | 206.8 | 208.5 |
| Boron | B | III | 10.91 | 11. |
| Bromin | Br | I | 79.32 | 79.96 |
| Cadmium | Cd | II | 111.5 | 112.4 |
| Cæsium | Cs | I | 131.94 | 133. |
| Calcium | Ca | II | 39.68 | 40. |
| Carbon | C | II, IV | 11.9 | 12. |
| Cerium | Ce | II, IV ($Ce_2$), vi | 138.89 | 140. |
| Chlorin | Cl | I | 35.17 | 35.45 |
| Chromium | Cr | II, IV ($Cr_2$), vi | 51.69 | 52.1 |
| Cobalt | Co | II, IV ($Co_2$), vi | 58.53 | 59. |
| Copper | Cu | II ($Cu_2$), ii | 63.09 | 63.6 |
| Erbium (?) | E | II ($E_2$), vi | 164.68 | 166. |
| Fluorin | F | I | 18.85 | 19. |
| Gallium | Ga | III ($Ga_2$), vi | 69.45 | 70. |
| Germanium | Ge | II, IV | 71.43 | 72. |
| Gold | Au | I, III | 195.63 | 197.2 |
| Helium | He | ? | 3.97 | 4. |
| Hydrogen | H | I | | 1.008 |
| Indium | In | II ($In_2$), vi | 113.1 | 114. |
| Iodin | I | I | 125.84 | 126.85 |
| Iridium | Ir | II, IV, VI | 191.47 | 193. |
| Iron | Fe | II, IV ($Fe_2$), vi | 55.56 | 56. |
| Lanthanum | La | III | 136.9 | 138. |
| Lead | Pb | II, IV | 205.06 | 206.9 |
| Lithium | Li | I | 6.97 | 7.03 |
| Magnesium | Mg | II | 24.17 | 24.36 |
| Manganese | Mn | II, IV ($Mn_2$), vi | 54.56 | 55. |
| Mercury | Hg | II ($Hg_2$), ii | 198.71 | 200.3 |
| Molybdenum | Mo | II, IV, VI | 95.24 | 96. |
| Neodym | Nd | II | 142.46 | 143.6 |
| Nickel | Ni | II, IV ($Ni_2$), vi | 58.23 | 58.7 |
| Niobium (Columbium) | Nb | V | 93.25 | 94. |

*The atomic weights O = 16 are those adopted by the Atomic Weight Commission of the German Chemical Society for 1900, and are used in this work. It is recommended that students use the nearest integral numbers: i. e., 23 for sodium; 108 for silver, etc.

ELEMENTS—continued

| NAME. | SYMBOL. | VALENCE. | ATOMIC WEIGHT H=1. | ATOMIC WEIGHT O=16. |
|---|---|---|---|---|
| Nitrogen | N | III, V | 13.93 | 14.04 |
| Osmium | Os | II, IV, VI | 189.48 | 191. |
| Oxygen | O | II | 15.87 | |
| Palladium | Pd | II, IV | 105.16 | 106. |
| Phosphorus | P | III, V | 30.74 | 31. |
| Platinum | Pt | II, IV | 193.25 | 194.8 |
| Potassium | K | I | 38.84 | 39.15 |
| Praseodym | Pr | II | 139.38 | 140.5 |
| Rhodium | Rh | II, IV | 102.18 | 103. |
| Rubidium | Rb | I | 84.72 | 85.4 |
| Ruthenium | Ru | II, IV, VI | 100.89 | 101.7 |
| Samarium | Sa | III, V | 148.81 | 150. |
| Scandium | Sc | III ($Sc_2$), vi | 43.75 | 44.1 |
| Selenium | Se | II, IV, VI | 78.47 | 79.1 |
| Silicon | Si | II, IV | 28.17 | 28.4 |
| Silver | Ag | I | 107.7 | 107.93 |
| Sodium | Na | I | 22.87 | 23.05 |
| Strontium | Sr | II, IV | 86.90 | 87.6 |
| Sulfur | S | II, IV, VI | 31.80 | 32.06 |
| Tantalum | Ta | III, V | 181.54 | 183. |
| Tellurium | Te | II, IV, VI | 126. | 127. |
| Thallium | Tl | I, III | 202.48 | 204.1 |
| Thorium | Th | IV | 230.65 | 232.5 |
| Tin | Sn | II, IV | 117.55 | 118.5 |
| Titanium | Ti | II, IV | 47.72 | 48.1 |
| Tungsten | W | II, IV, VI | 182.54 | 184. |
| Uranium | U | II, IV ($U_2$), vi | 237.60 | 239.5 |
| Vanadium | V | III, V ($V_2$), vi | 50.80 | 51.2 |
| Ytterbium | Yb | III | 171.62 | 173. |
| Ytterium | Y | III | 88.29 | 89. |
| Zinc | Zn | II | 64.88 | 65.4 |
| Zirconium | Zr | II, IV | 90.00 | 90.7 |

In some cases the results of analyses are such as would agree with two values as the atomic weight equally well. In this case we can decide which is the correct value by the law of Dulong and Petit: The product of the specific heat (p. 19) of any solid element into its atomic weight is approximately a constant number. This number, known as the atomic heat, varies between 5.39 and 6.87. When the chemical relations indicate either one of two numbers as the atomic weight, that one is selected which, when multiplied by the specific heat, gives an atomic heat within the above limits.

The atomic heats of those elements which exist in two or more allotropic modifications (p. 12) vary in the several forms, and at different temperatures, and fall outside of the above limits. Thus the atomic heat of crystallized boron is 2.11 at $-39.6°$, and 3.99 at 233.2°, while that of amorphous boron is 2.81; that of the diamond is 0.76 at $-50.5°$, and 5.51 at 985°, while that of graphite is 1.37 at $-50.3°$, and 5.60 at 978°.

**Molecular Weight.—The molecular weight of a substance is the weight of its molecule as compared with the weight of an atom of hydrogen.** It is also, obviously, the sum of the weights of all the atoms making up the molecule.

A very ready means of determining the molecular weight of a gaseous substance or of one which may be converted into vapor, is based upon Avogadro's law. The sp. gr. of a gas is the weight of a given volume as compared with that of an equal volume of hydrogen. But these equal volumes contain equal numbers of molecules (p. 34), and therefore, in determining the sp. gr. of a gas, we obtain the weight of its molecule as compared with that of a molecule of hydrogen; and, as the molecule contains two atoms of hydrogen, while one atom of hydrogen is the unit of comparison, it follows that **the specific gravity of a gas compared with hydrogen, multiplied by two, is its molecular weight.**

For example, the gas acetylene and the liquid benzene each contain 92.31 per cent of carbon, and 7.69 per cent of hydrogen; which is equivalent to 24 parts, or two atoms of carbon; and 2 parts, or two atoms of hydrogen. The sp. gr. of acetylene, referred to hydrogen = 2, is 13; its molecular weight is, therefore, 26, and its molecule contains two atoms of carbon and two atoms of hydrogen. The sp. gr. of vapor of benzene is 39; its molecular weight is, therefore, 78, and its molecule contains six atoms of carbon and six atoms of hydrogen.

When a substance is not capable of being volatilized, its molecular weight may be obtained from certain properties of its solutions, which will be considered in connection with organic chemistry (see p. 221).

The vapor densities of comparatively few elements are known:

| | Vapor Density. | Atomic Weight. | Molecular Weight. |
|---|---|---|---|
| Hydrogen | 1 | 1 | 2 |
| Oxygen | 16 | 16 | 32 |
| Sulfur | 32 | 32 | 64 |
| Selenium | 82 | 79 | 164 |
| Tellurium | 130 | 128 | 260 |
| Chlorin | 35.5 | 35.5 | 71 |
| Bromin | 80 | 80 | 160 |
| Iodin | 127 | 127 | 254 |
| Phosphorus | 63 | 31 | 124 |
| Arsenic | 150 | 75 | 300 |
| Nitrogen | 14 | 14 | 28 |
| Potassium | 39 | 39 | 78 |
| Cadmium | 56 | 112 | 112 |
| Mercury | 100 | 200 | 200 |

The atomic weight being, in most of the above instances, equal to the vapor density, and to half the molecular weight, it may be

inferred that *the molecules of these elements consist of two atoms.* Noticeable discrepancies exist in the case of four elements. The molecular weights of phosphorus and arsenic, as obtained from their vapor densities, are not double, but four times as great as their atomic weights. The molecules of phosphorus and arsenic are, therefore, supposed to contain four atoms. Those of cadmium, zinc and mercury contain but one atom.

**Valence or atomicity.**—It is known that the atoms of different elements possess different powers of combining with and of replacing atoms of hydrogen. Thus:

1 atom of chlorin combines with 1 atom of hydrogen.
1 atom of oxygen combines with 2 atoms of hydrogen.
1 atom of nitrogen combines with 3 atoms of hydrogen.
1 atom of carbon combines with 4 atoms of hydrogen.

**The valence, atomicity, or equivalence of an element is the saturating power of one of its atoms as compared with that of one atom of hydrogen.**

Elements may be classified according to their valence into—

Univalent elements, or monads . . . . . Cl′
Bivalent elements, or dyads . . . . . O″
Trivalent elements, or triads . . . . . B‴
Quadrivalent elements, or tetrads . . . . . Civ
Quinquivalent elements, or pentads . . . . . Pv
Sexvalent elements, or hexads . . . . . Wvi

Elements of even valence, i. e., those which are bivalent, quadrivalent, or sexvalent, are sometimes called **artiads**; those of uneven valence being designated as **perissads.**

In notation the valence is indicated, as above, by signs placed to the right and above the symbol of the element.

But the valence of the elements is not fixed and invariable. Thus, while chlorin and iodin each combine with hydrogen, atom for atom, and in those compounds are consequently univalent, they unite with each other to form two compounds—one containing one atom of iodin and one of chlorin, the other containing one atom of iodin and three of chlorin. Chlorin being univalent, iodin is obviously trivalent in the second of these compounds. Again, phosphorus forms two chlorids, one containing three, the other five atoms of chlorin to one of phosphorus.

In view of these facts, we must consider either: 1, That the valence of an element is that which it exhibits in its most saturated compounds, as phosphorus in the pentachlorid, and that the lower compounds are non-saturated, and have free valences; or 2, that the valence is variable. The first supposition depends too much

upon the chances of discovery of compounds in which the element has a higher valence than that which might be considered the maximum to-day. The second supposition — notwithstanding the fact that, if we admit the possibility of two distinct valences, we must also admit the possibility of others — is certainly the more tenable and the more natural. *In speaking, therefore, of the valence of an element, we must not consider it as an absolute quality of its atoms, but simply as their combining power in the particular class of compounds under consideration.* Indeed, compounds are known in whose molecules the atoms of one element exhibit two distinct valences. Thus, ammonium cyanate contains two atoms of nitrogen: one in the ammonium group is quinquivalent, one in the acid radical is trivalent.

When an element exhibits different valences, these differ from each other by two. Thus, phosphorus is trivalent or quinquivalent; platinum is bivalent or quadrivalent.

**The chemical equivalent, or equivalent weight,** of an element is the weight of that element capable of combining with unit weight of hydrogen (or chlorin). It is, therefore, its atomic weight divided by its valence. We have seen (p. 35) that 35.5 parts by weight of chlorin combine with 1 part by weight of hydrogen, 16 of oxygen with 2 of hydrogen, and 14 of nitrogen with 3 of hydrogen. Chlorin being univalent, oxygen bivalent and nitrogen trivalent, their equivalent weights are, therefore, respectively: $35.5 \div 1 = 35.5$, $16 \div 2 = 8$, and $14 \div 3 = 4.67$.

**Symbols, Formulæ, Equations.— Symbols** are conventional abbreviations of the names of the elements, whose purpose it is to introduce simplicity and exactness into descriptions of chemical actions. They consist of the initial letter of the Latin name of the element, to which is usually added one of the other letters. If there be more than two elements whose names begin with the same letter, the single-letter symbol is reserved for the commonest element. Thus, we have nine elements whose names begin with C; of these the commonest is Carbon, whose symbol is C; the others have double-letter symbols, as Chlorin, Cl; Cobalt, Co; Copper, Cu (Cuprum), etc.

**These symbols do not indicate simply an indeterminate quantity, but represent one atom of the corresponding element.**

When more than one atom is spoken of, the number of atoms which it is desired to indicate is written either before the symbol or, in small figures, after and below it. Thus, H indicates one atom of hydrogen; 2Cl, two atoms of chlorin; $C_4$, four atoms of carbon, etc.

What the symbol is to the element, the **formula** is to the compound. By it the number and kind of atoms of which the molecule

of a substance is made up are indicated. The simplest kind of formulæ are what are known as **empirical formulæ**, which indicate only the kind and number of atoms which form the compound. Thus, HCl indicates a molecule composed of one atom of hydrogen united with one atom of chlorin; $5H_2O$, five molecules, each composed of two atoms of hydrogen and one atom of oxygen, the number of molecules being indicated by the proper numeral placed before the formula, in which place it applies to all the symbols following it. Sometimes it is desired that a numeral shall apply to a part of the symbols only, in which case they are enclosed in parentheses; thus, $Al_2(SO_4)_3$ means twice Al and three times $SO_4$.

For other varieties of formulæ, see pp. 54, 55.

**Equations** are combinations of formulæ and algebraic signs so arranged as to indicate a chemical reaction and its results. The signs used are the plus and equality signs; the former being equivalent to "and," and the second meaning "have reacted upon each other and have produced." The substances entering into the reaction are placed before the equality sign, and the products of the reaction after it; thus, the equation

$$2KHO+H_2SO_4=K_2SO_4+2H_2O$$

means, when translated into ordinary language: two molecules of potash, each composed of one atom of potassium, one atom of hydrogen, and one atom of oxygen, *and* one molecule of sulfuric acid, composed of two atoms of hydrogen, one atom of sulfur, and four atoms of oxygen, *have reacted upon each other and have produced* one molecule of potassium sulfate, composed of two atoms of potassium, one atom of sulfur, and four atoms of oxygen, *and* two molecules of water, each composed of two atoms of hydrogen and one atom of oxygen.

**As no material is ever lost or created in a reaction, the number of each kind of atom occurring before the equality sign in an equation must always be the same as that occurring after it.** In writing equations they should always be proved by examining whether the half of the equation before the equality sign contains the same number of each kind of atom as that after the equality sign. If it do not the equation is incorrect.

The word "reaction" is used in chemistry in two distinct meanings: As applying to the action mentioned above, it refers to the mutual action of two substances upon each other. In the other meaning it refers to the action of substances upon certain organic pigments. Thus, the **reaction** of a substance is **acid**, when it turns blue litmus red; **alkaline**, when it turns reddened litmus blue, and **neutral**, when it has no action upon either blue or red litmus.

**Acids, Bases, and Salts.**—All ternary and quarternary mineral substances have one of three functions.

The function of a substance is its chemical character and relationship, and indicates certain general properties, reactions and decompositions which all substances possessing the same function possess or undergo alike. Thus, in mineral chemistry we have **acids, bases,** and **salts**; in organic chemistry alcohols, aldehydes, ketones, ethers, etc.

**An acid is a compound of an electro-negative element or residue with hydrogen; which hydrogen it can part with in exchange for an electro-positive element without formation of a base.** An acid has also been defined as a compound body which evolves water by its action upon pure caustic potash or soda. This latter definition is undesirable, in view of the existence of certain zinc and aluminium compounds (pp. 193, 198).

No substance which does not contain hydrogen can, therefore, be called an acid.

**The basicity of an acid is the number of replaceable hydrogen atoms contained in its molecule.**

**A monobasic** acid is one containing a single replaceable atom of hydrogen, as nitric acid, $HNO_3$; a **dibasic** acid is one containing two such replaceable atoms, as sulfuric acid, $H_2SO_4$; a **tribasic** acid is one containing three replaceable hydrogen atoms, as phosphoric acid, $H_3PO_4$. **Polybasic** acids are such as contain more than one atom of replaceable hydrogen.

**Hydracids** are acids containing no oxygen; **oxacids** or **oxyacids** contain both hydrogen and oxygen.

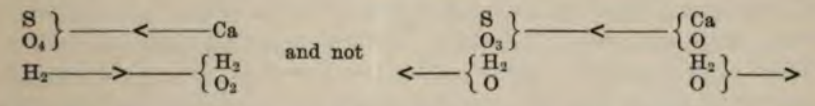
The term **base** is regarded by many authors as applicable to any compound body capable of neutralizing an acid. It is, however, more consistent with modern views to limit the application of the name to such **ternary compound substances as are capable of entering into double decomposition with acids to form salts and water.** They may be considered as one or more molecules of water in which one-half of the hydrogen has been replaced by an electro-positive element or radical; or as compounds of such elements or radicals with one or more groups, OH. Being thus considered as derivable from water, they are also known as **hydroxids.** They have the general formula, $M_n(OH)_n$. They are **monatomic, diatomic, triatomic,** etc., according as they contain one, two, three, etc., groups **oxhydryl,** or **hydroxyl** (OH). As acids having one, two or three, etc., atoms of replaceable hydrogen are designated as monobasic, dibasic, or tribasic acids, etc., so bases having one replaceable hydroxyl are spoken of as **monacid bases,** those having two as **diacid bases,** etc.

**The atomicity of a compound is the number of oxhydryls in its molecule, which it may lose by their combination with the hydrogen of acids.**

**A double decomposition is a reaction in which both of the reacting compounds are decomposed to form two new compounds.**

**Thiobases,** or hydrosulfids, are compounds in all respects resembling the bases, except that in them the oxygen of the base is replaced by sulfur.

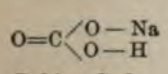
**Salts are substances formed by the substitution of basylous radicals or elements for a part or all of the replaceable hydrogen of acids.** They are always formed, therefore, when bases and acids enter into double decomposition. They are not, as was formerly supposed, formed by the union of a metallic with a non-metallic oxid, but, as stated above, by the substitution of one or more atoms of an element or radical for the hydrogen of the acid. Thus, the compound formed by the action of sulfuric acid upon slaked lime is not $SO_3CaO$, but $CaSO_4$, formed by the interchange of atoms:



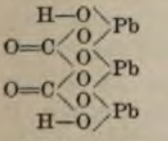

it is therefore, **calcium sulfate,** and not **sulfate of lime.**

As salts are produced by double decomposition between acids and bases the latter play as much part in the formation of salts as do the former, and we may also consider the salts as **substances formed by the substitution of acid residues** (p. 53) **for a part or all of the oxhydryl of bases.**

It will be seen from the above that in some salts the hydrogen of the acid is only partly replaced, as in baking soda. Such salts are called **bi salts** or **acid salts.** There exist, also, salts in which a portion of the oxhydryl of the bases is retained, as white lead. Such salts are called **basic salts** (See p. 52).



Baking Soda.



White Lead.

The term **salt,** as used at present, applies to the compounds formed by the substitution of a basylous element for the hydrogen of *any* acid; and indeed, as used by some authors, to the acids themselves, which are considered as salts of hydrogen. It is probable, however, that eventually the name will be limited to such compounds as correspond to acids whose molecules contain more than two elements. Indeed, from the earliest times of modern chemistry a distinction has been observed between the **haloid salts,** i. e., those the molecules of whose corresponding acids consist

of hydrogen, united with one other element, on the one hand; and **the oxysalts,** the salts of the oxacids, i. e., those into whose composition oxygen enters, on the other hand. This distinction, however, has gradually fallen into the background, for the reason that the methods and conditions of formation of the two kinds of salts are usually the same *when the basylous element belongs to that class usually designated as metallic.*

There are, however, important differences between the two classes of compounds. There exist compounds of all of the elements corresponding to the hydracids, binary compounds of chlorin, bromin, iodin, and sulfur. There is, on the other hand, a large class of elements the members of which are incapable of forming salts corresponding to the oxacids. No salt of an oxacid with any one of the elements usually classed as metalloids (excepting hydrogen) has been obtained.

Haloid salts may be formed by direct union of their constituent elements; oxysalts are never so produced.

**Ionization—Electrolytic Dissociation.**—It has been stated (pp. 29, 30) that substances in solution which are conductors of electricity are decomposed into their constituent ions, and that these exist in the solutions in greater or lesser amount. The ions are, moreover, the conductors of the currents, and therefore the conductivity of a given solution depends upon the number of free ions which it contains; upon the extent to which ionization has taken place in the solution. In considering the relative conductivity of substances in solution, comparison is made between molecular solutions or equivalent solutions, not percentage solutions, and the conductivity is referred to as **molecular conductivity,** or **equivalent conductivity.** Thus comparisons are made, not with solutions containing, for example, 10 p/m of hydrochloric acid and of sulfuric acid, but containing 36.5 HCl and 98 $H_2SO_4$ per litre for molecular, or 36.5 HCl and 49 $H_2SO_4$ for equivalent conductivity. Molecular conductivity ($\mu$) is therefore a measure of ionization, and as it increases with increase of temperature and with dilution, electrolytic dissociation varies correspondingly. The influence of dilution is greater with some substances than with others. Thus, considering the molecular conductivity of hydrochloric acid in a m/10 solution at 20° as unity, those of sulfuric acid and acetic acid are 0.5 and 0.012 for solutions of like molecular concentration. On diluting to m/100 the values become 1, 0.7 and 0.05; and at m/1000: 1, 0.9 and 0.12. The molecular conductivity of hydrochloric acid varies very slightly with dilution: 0.95 at m/10, 0.99 at m/1000, while that of acetic acid is increased ten times by similar dilution. There is also a limit to the increase of molecular conductivity by dilution, and it is believed that this limit is reached when dissociation is complete.

It is inferred from these facts that at m/10 the ionization of hydrochloric acid is almost complete, while at that dilution the solution of acetic acid contains relatively few free ions. This explains why one acid is "stronger" than another. If equal volumes of eq./10 solutions of hydrochloric, sulfuric and acetic acids are acted upon by equal quantities of a given metal, zinc for example, the quantity of hydrogen liberated from each, and of metal dissolved by each, will be the same, and in that regard the equivalent quantities of the three acids equal each other. But if the time consumed by the reactions be considered the three acids will be found to differ in **chemical activity**; hydrochloric acid acting the most rapidly and acetic acid the most slowly. It will also be observed that in chemical activity they vary in the same manner as they vary in molecular conductivity, i. e., in proportion to the extent of their electrolytic dissociation; and that acid is the strongest, i. e., has the greatest chemical activity, whose solution contains the largest proportion of free ions.

The explanation of other important chemical phenomena is also furnished by the hypothesis of ionization. We have seen that the characterizing quality of the hydrogen of acids is that it is replaceable by electropositive elements (metals), and that the hydroxyl of bases is likewise replaceable by the residues of acids. These are properties which are peculiar to the hydrogen atom and the hydroxyl *in these forms of combination*, and many other compounds are known containing hydrogen atoms and hydroxyl groups which are not replaceable in such manner. These marked differences in the properties of hydrogen atoms (and of hydroxyl groups) contained in solutions of acids (or of alkalies) from those possessed by them when in the form of free hydrogen or in other forms of combination, are considered to be due to their existence as ions in such solutions. And, furthermore, the acid qualities of the hydrogen in acids are only manifested in solutions.

In the usual methods of qualitative analysis of mineral salts the first step is to bring the substance into solution. This having been done, the salt is considered as made up of two factors, a basic and an acid one, which are separately identified. Thus, in a solution containing zinc chlorid and copper sulfate, the presence of the zinc and copper is first discovered by one series of operations, and that of the chlorin and sulfuric acid residue by another. The principle underlying this method of procedure is that in all their forms of combination in acid, base or salt, the basic and acidulous factors each have certain definite reactions, irrespective of the nature of the other factor present. Thus all dissolved metallic chlorids and hydrochloric acid give a white precipitate with silver nitrate solution, whatever the metal may be; and all dissolved saline compounds of

copper give a black precipitate with hydrogen sulfid in acid solution, whatever the acid may be. These facts are explained by the supposition that the solutions of acids, bases and salts contain the free ions; that solution of hydrochloric acid contains the ions H and Cl, and that of copper sulfate the ions Cu and $SO_4$, etc.; and that on addition of a solution of silver nitrate to a solution of zinc chlorid the ion Ag of the former combines with ion Cl of the latter, while the ions Zn and $SO_4$ also combine to form $ZnSO_4$.

**Action of Acids and Bases on Salts, and of Salts on each other.** — (1) If an acid be added to a solution of a salt whose acid it nearly equals in chemical activity, the salts of both acids and the acids themselves will probably exist in the solution, provided both acids and salts are soluble. Thus, if sulfuric acid be added to a solution of potassium nitrate, the solution will contain potassium sulfate and nitrate, and sulfuric and nitric acid: $2H_2SO_4 + 3KNO_3 = K_2SO_4 + KNO_3 + H_2SO_4 + 2HNO_3$.

(2) If an acid be added to a solution of a salt whose acid it greatly exceeds in activity, the salt is decomposed, with formation of the salt of the stronger acid, and liberation of the weaker acid, both salts and acids being soluble. Thus, if sulfuric acid be added to a solution of sodium acetate, the solution will contain sodium sulfate and acetic acid: $H_2SO_4 + 2NaC_2H_3O_2 = Na_2SO_4 + 2HC_2H_3O_2$.

(3) When solutions of two salts, the acids of both of which form soluble salts with both bases, are mixed the resultant liquid contains the four salts. Thus, if potassium sulfate and sodium nitrate be dissolved in the same solution it will contain potassium and sodium sulfates and potassium and sodium nitrates: $3K_2SO_4 + 3NaNO_3 = 2K_2SO_4 + Na_2SO_4 + 2KNO_3 + NaNO_3$, or in some other proportion.

In the light of the hypothesis of ionization, the statements 1, 2 and 3, while applying to that portion of the compounds which remain un-ionized, may be better expressed in the one: Solutions of acids, bases and salts contain all the free ions. Thus, in the example given in 3, the solution contains K, Na, $SO_4$, and $NO_3$.

(4) If to a solution of a salt, whose acid is insoluble in the solvent used, an acid be added, capable of forming a soluble salt with the basylous element, such soluble salt is formed and the acid is deposited. Thus, if sulfuric acid be added to an aqueous solution of sodium stearate, stearic acid will be deposited and sodium sulfate formed: $H_2SO_4 + 2NaC_{18}H_{35}O_2 = Na_2SO_4 + 2HC_{18}H_{35}O_2$.

(5) If, to a solution of a salt, an acid be added which is capable of forming an insoluble salt with the base, such insoluble salt is formed and precipitated. Thus, if sulfuric acid be added to a solution of barium nitrate, barium sulfate is precipitated and nitric acid liberated: $H_2SO_4 + Ba(NO_3)_2 = BaSO_4 + 2HNO_3$.

(6) If to a solution of a salt whose basylous element is insoluble a soluble base be added, capable of forming a soluble salt with the acid, such soluble salt is formed, with precipitation of the insoluble base. Thus, if potassium hydroxid be added to a solution of cupric sulfate, cupric hydroxid is precipitated and potassium sulfate formed: $2KHO + CuSO_4 = Cu(HO)_2 + K_2SO_4$.

(7) If a base be added to a solution of a salt with whose acid it is capable of forming an insoluble salt, such insoluble salt is formed and precipitated, and the base of the original salt, if insoluble, is also precipitated. Thus if solutions of barium hydroxid and of potassium sulfate be mixed, barium sulfate is precipitated and the solution contains potassium hydroxid: $Ba(HO)_2 + K_2SO_4 = BaSO_4 + 2KHO$; or if solutions of barium hydroxid and silver sulfate be mixed both barium sulfate and silver hydroxid will be precipitated: $Ba(HO)_2 + Ag_2SO_4 = BaSO_4 + 2AgHO$, and if the substances be used in the proportions given in the equation pure water will remain.

(8) If solutions of two salts, the acid of one of which is capable of uniting with the base of the other to form an insoluble salt, be mixed, such insoluble salt is precipitated. Thus, if solutions of barium nitrate and of sodium sulfate be mixed, barium sulfate is precipitated and sodium nitrate formed: $Ba(NO_3)_2 + Na_2SO_4 = BaSO_4 + 2NaNO_3$.

The statements 4 to 8 may be summarized in the statement: When solutions of acids, bases or salts any of whose ions are capable of uniting to form an insoluble compound are mixed, such insoluble compound is formed and precipitated.

(9) If to a salt whose acid is volatile at the existing temperature, an acid capable of forming with the basylous element a salt fixed at the same temperature be added, the fixed salt is formed and the volatile acid expelled. Thus, with the application of heat, sulfuric acid expels nitric acid from sodium nitrate to form sodium sulfate: $H_2SO_4 + 2NaNO_3 = 2HNO_3 + Na_2SO_4$.

(10) Similarly, a volatile base is expelled from its salts by a fixed one. Thus caustic potash and ammonium chlorid form ammonia, water and potassium chlorid: $KHO + NH_4Cl = KCl + NH_3 + H_2O$.

**Stoichiometry** (στοιχεῖον=an element; μέτρον=a measure)—in its strict sense refers to the law of definite proportions, and to its applications. In a wider sense, the term applies to the mathematics of chemistry, to those mathematical calculations by which the quantitative relations of substances acting upon each other, and of the products of such reactions are determined.

A chemical reaction can always be expressed by an equation, which, as it represents not only the nature of the materials involved, but also the number of molecules of each, is a quantitative as well as a qualitative statement.

Let it be desired to determine how much sulfuric acid will be required to completely decompose 100 parts of sodium nitrate, and what will be the nature and quantities of the products of the decomposition. First the equation representing the reaction is constructed:

| $H_2SO_4$ | + | $2NaNO_3$ | = | $Na_2SO_4$ | + | $2HNO_3$ |
|---|---|---|---|---|---|---|
| Sulfuric acid. | | Sodium nitrate. | | Disodic sulfate. | | Nitric acid. |

which shows that one molecule of sulfuric acid decomposes two molecules of sodium nitrate, with the formation of one molecule of sodium sulfate and two of nitric acid. The quantities of the different substances are, therefore, represented by their molecular weights, or some multiple thereof, which are in turn obtained by adding together the atomic weights of the constituent atoms:

| $H_2SO_4$ | + | $2NaNO_3$ | = | $Na_2SO_4$ | + | $2HNO_3$ |
|---|---|---|---|---|---|---|
| $1\times2=2$ | | $23\times1=23$ | | $23\times2=46$ | | $1\times1=1$ |
| $32\times1=32$ | | $14\times1=14$ | | $32\times1=32$ | | $14\times1=14$ |
| $16\times4=64$ | | $16\times3=48$ | | $16\times4=64$ | | $16\times3=48$ |
| 98 | | $85\times2=170$ | | 142 | | $63\times2=126$ |

Consequently, 98 parts $H_2SO_4$ decompose 170 parts $NaNO_3$, and produce 142 parts $Na_2SO_4$, and 126 parts $HNO_3$. To find the result as referred to 100 parts $NaNO_3$, we apply the simple proportion:

$170 : 100 :: 98 : 57.64 - 57.64 =$ parts $H_2SO_4$ required.
$170 : 100 :: 142 : 83.53 - 83.53 =$ " $Na_2SO_4$ produced.
$170 : 100 :: 126 : 74.11 - 74.11 =$ " $HNO_3$ "

As in writing equations (see p. 41), the work should always be proved by adding together the quantities on each side of the equality sign, which should equal each other: $98+170=268=142+126=268$, or $57.64 + 100 = 157.64 = 83.53 + 74.11 = 157.64$.

In determining quantities as above, regard must be had to the purity of the reagents used, and, if they be crystallized, to the amount of water of crystallization (see p. 12) they contain.

Let it be desired to determine how much crystallized cupric sulfate can be obtained from 100 parts of sulfuric acid of 92 per cent strength. As cupric sulfate crystallizes with five molecules of water of crystallization the reaction occurs according to the equation:

| $H_2SO_4$ | + | $CuO$ | + | $4H_2O$ | = | $CuSO_4 5Aq.$ |
|---|---|---|---|---|---|---|
| Sulfuric acid. | | Cupric oxid. | | Water. | | Cupric sulfate. |
| | | 63 | | $1\times2=2$ | | $63\times1=63$ |
| $1\times2=2$ | | 16 | | $16\times1=16$ | | $32\times1=32$ |
| $32\times1=32$ | | | | | | $16\times4=64$ |
| $16\times4=64$ | | | | | | $18\times5=90$ |
| 98 | | 79 | | $18\times4=72$ | | 249 |

$98 + 79 + 72 = 249$

98 parts of 100 per cent $H_2SO_4$ will produce, therefore, 249 parts of crystallized cupric sulfate. But as the acid liquid used contains only 92 parts of true $H_2SO_4$, in 100; 100 parts of such acid will yield 233.75 parts of crystallized sulfate, for 98:92::249:233.75.

In gravimetric quantitative analysis the substance whose quantity is to be determined is converted into an insoluble compound, which is then purified, dried, and weighed, and from this weight the desired result is calculated.

Let the problem be to determine what percentage of silver is contained in a silver coin. Advantage is taken of the formation of the insoluble silver chlorid. A piece of the coin is chipped off and weighed: weight of coin used = 2.5643 grams. The chip is then dissolved in nitric acid, forming a solution of silver nitrate. From this solution the silver is precipitated as chlorid, by the addition of hydrochloric acid, according to the equation:

| $AgNO_3$ | + | HCl | = | AgCl | + | $HNO_3$ |
|---|---|---|---|---|---|---|
| Silver nitrate. | | Hydrochloric acid. | | Silver chlorid. | | Nitric acid. |
| $108\times1=108$ | | 1 | | 108 | | $1\times1=1$ |
| $14\times1=14$ | | 35.5 | | 35.5 | | $14\times1=14$ |
| $16\times3=48$ | | | | | | $16\times3=48$ |
| 170 | | 36.5 | | 143.5 | | 63 |

$$170+36.5=206.5=143.5+63.$$

The silver chlorid is collected, dried and weighed:

| | |
|---|---|
| Weight of coin used | 2.5643 grams. |
| Weight of AgCl obtained | 3.0665 " |

as 143.5 grams AgCl contain 108 grams Ag—143.5:108::3.0665:2.3078—2.5643 grams of the coin contain 2.3078 grams of silver, or 90 per cent—2.5643:100::2.3078:90.

**Nomenclature.**—The names* of the elements are mostly of Greek derivation, and have their origin in some prominent property of the substance. Thus, *phosphorus*, φῶς, *light*, and φέρειν, *to bear*. Some are of Latin origin, as *silicon*, from *silex*, flint; some of Gothic origin, as *iron*, from *iarn;* and others are derived from modern languages, as *potassium* from *pot-ash*. Very little system has been followed in naming the elements, beyond applying the termination *ium* to the metals, and *in* or *on* to the non-metals; and even to this rule we find such exceptions as a metal called *manganese* and a non-metal called *sulfur*.

The names of *compound substances* were formerly chosen upon the same system, or rather lack of system, as those of the elements.

*For rules governing orthography and pronunciation of chemical terms, see Appendix A.

So long as the number of compounds with which the chemist had to deal remained small, the use of these fanciful appellations, conveying no more to the mind than perhaps some unimportant quality of the substances to which they applied, gave rise to comparatively little inconvenience. In these later days, however, when the number of compounds known to exist, or whose existence is shown by approved theory to be possible, is practically infinite, some systematic method of nomenclature has become absolutely necessary.

**The principle of the system of nomenclature at present used is that the name shall convey the composition and character of the substance.**

Compounds consisting of two elements, or of an element and a radical only, *binary compounds*, are designated by compound names made up of the name of the more electro-positive, followed by that of the more electro-negative, in which the termination *id* has been substituted for the termination *in*, *on*, *ogen*, *ygen*, *orus*, *ium*, and *ur*. For example: the compound of potassium and chlorin is called potassium chlor*id*, that of potassium and oxygen potassium ox*id*, that of potassium and phosphorus potassium phosph*id*.

In a few instances the older name of a compound is used in preference to the one which it should have under the above rule, for the reason that the substance is one which is typical of a number of other substances, and therefore deserving of exceptional prominence. Such are *ammonia*, $NH_3$; *water*, $H_2O$.

When, as frequently happens, two elements unite with each other to form more than one compound, these are usually distinguished from each other by prefixing to the name of the element varying in amount the Greek numeral corresponding to the number of atoms of that element, as compared with a *fixed* number of atoms of the other element.

Thus, in the series of compounds of nitrogen and oxygen, most of which contain two atoms of nitrogen, $N_2$ is the standard of comparison, and consequently the names are as follows:

| | |
|---|---|
| $N_2O$ | = Nitrogen *mon*oxid. |
| NO $(= N_2O_2)$ | = Nitrogen *di*oxid. |
| $N_2O_3$ | = Nitrogen *tri*oxid. |
| $NO_2$ $(= N_2O_4)$ | = Nitrogen *tetr*oxid. |
| $N_2O_5$ | = Nitrogen *pent*oxid. |

Another method of distinguishing two compounds of the same two elements consists in terminating the first word in *ous* in that compound which contains the less proportionate quantity of the more electro-negative element, and in *ic* in that containing the greater proportion; thus:

$SO_2$ = Sulfur*ous* oxid.
$SO_3$ = Sulfur*ic* oxid.

$Hg_2Cl_2$ (2Hg : 2Cl) = Mercur*ous* chlorid.
$HgCl_2$ (2Hg : 4Cl) = Mercur*ic* chlorid.

This method, although used to a certain extent in speaking of compounds composed of two elements of Class II (see p. 57), is used chiefly in speaking of binary compounds of elements of different classes.

In naming the *oxacids* the word *acid* is used, preceded by the name of the electro-negative element other than oxygen, to which a prefix or suffix is added to indicate the degree of oxidation. If there be only two, the least oxidized is designated by the suffix *ous*, and the more oxidized by the suffix *ic*, thus:

$HNO_2$ = Nitr*ous* acid.
$HNO_3$ = Nitr*ic* acid.

If there be more than two acids, formed in regular series, the least oxidized is designated by the prefix *hypo* and the suffix *ous;* the next by the suffix *ous;* the next by the suffix *ic;* and the most highly oxidized by the prefix *per* and the suffix *ic;* thus:

$HClO$ = *Hypo*chlor*ous* acid.
$HClO_2$ = Chlor*ous* acid.
$HClO_3$ = Chlor*ic* acid.
$HClO_4$ = *Per*chlor*ic* acid.

Certain elements, such as sulfur and phosphorus, exist in acids which are derived from those formed in the regular way, and which are specially designated.

The names of the oxysalts are derived from those of the acids by dropping the word *acid*, changing the termination of the other word from *ous* into *ite*, or from *ic* into *ate*, and prefixing the name of the electro-positive element or radical; thus:

| | |
|---|---|
| $HNO_2$ | $KNO_2$ |
| Nitr*ous* acid. | Potassium nitr*ite*. |
| $HNO_3$ | $KNO_3$ |
| Nitr*ic* acid. | Potassium nitr*ate*. |
| $HClO$ | $KClO$ |
| Hypochlor*ous* acid. | Potassium hypochlor*ite*. |

Acids whose molecules contain more than one atom of replaceable hydrogen are capable of forming more than one salt with electro-positive elements, or radicals, whose valence is less than the basicity of the acid. Ordinary phosphoric acid, for instance, contains in each molecule three atoms of basic hydrogen, and consequently is capable

of forming three salts by the replacement of one, two, or three of its hydrogen atoms, by one, two, or three atoms of a univalent metal. To distinguish these the Greek prefixes *mono*, *di*, and *tri* are used, the termination *ium* of the name of the metal being changed to *ic*, thus:

$H_2KPO_4$ = *Mono*potass*ic* phosphate.
$HK_2PO_4$ = *Di*potass*ic* phosphate.
$K_3PO_4$ = *Tri*potass*ic* phosphate.

The first is also called *dihydro*potass*ic* phosphate, and the second, *hydrodi*potass*ic* phosphate.

In the older works, salts in which the hydrogen has not been entirely displaced are sometimes called **bisalts** (bicarbonates), or **acid salts**; those in which the hydrogen has been entirely displaced being designated as **neutral salts.**

Some elements, such as mercury, copper, and iron, form two distinct series of salts. These are distinguished, in the same way as the acids, by the use of the suffix *ous* in the names of those containing the less proportion of the electro-negative group, and the suffix *ic* in those containing the greatest proportion, e. g.:

$(Cu_2)SO_4$ . . . . . ($1SO_4 : 2Cu$) = Cupr*ous* sulfate.
$CuSO_4$ . . . . . ($2SO_4 : 2Cu$) = Cupr*ic* sulfate.

$FeSO_4$ . . . . . ($2SO_4 : 2Fe$) = Ferr*ous* sulfate.
$(Fe_2)(SO_4)_3$ . . . . . ($3SO_4 : 2Fe$) = Ferr*ic* sulfate.

The names, **basic salts, subsalts** and **oxysalts** have been applied indifferently to salts, such as the lead subacetates, which are compounds containing the normal acetate and the hydroxid or oxid of lead; and to salts such as the so-called bismuth subnitrate, which is a nitrate, not of bismuth, but of the univalent radical $(Bi'''O'')'$.

By **double salts** are meant such as are formed by the substitution of different elements or radicals for two or more atoms of replaceable hydrogen of the acid, such as ammonio-magnesian phosphate, $PO_4Mg''$ $(NH_4)'$.

**Radicals.**—Many compounds contain groups of atoms which pass from one compound to another, and, in many reactions, behave like elementary atoms. Such groups are called **radicals**, or **compound radicals.**

Marsh gas has the composition $CH_4$. By acting upon it in suitable ways we can cause the atom of carbon, accompanied by three of the hydrogen atoms, to pass into a variety of other compounds, such as $(CH_3)Cl$, $(CH_3)OH$, $(CH_3)_2O$, $C_2H_3O_2$ $(CH_3)$. Marsh gas, therefore, consists of the radical $(CH_3)$ combined with an atom of hydrogen: $(CH_3)'H$.

It is especially among the compounds of carbon that the existence

of radicals comes into prominent notice. They, however, occur in inorganic substances also. Thus the nitric acid molecule consists of the radical $NO_2$, combined with the group OH.

Like the elements, the radicals possess different valences, depending upon the number of unsatisfied valences which they contain. Thus the radical ($CH_3$) is univalent, because three of the four valences of the carbon atom are satisfied by atoms of hydrogen, leaving one free valence. The radical (PO) of phosphoric acid is trivalent, because two of the five valences of the phosphorus atom are satisfied by the two valences of the bivalent oxygen atom, leaving three free valences.

In notation the radicals are usually enclosed in brackets as above, to indicate their nature. The names of radicals terminate in *yl* or in *gen;* thus: ($CH_3$) = methyl; (CN) = cyanogen.

The terms *radical* and *residue* are not synonymous. In speaking of acids their *radicals* are obtained by the subtraction of a number of hydroxyls equal to the basicity of the acid. Thus: $HNO_3 - HO = NO_2$; $H_2SO_4 - 2HO = SO_2$; $H_3PO_4 - 3HO = PO$. The *residue* is that which remains after removal of the basic, or replaceable, hydrogen. Thus: $HNO_3 - H = NO_3$; $H_2SO_4 - H_2 = SO_4$; $H_3PO_4 - H_3 = PO_4$. (See Electrolysis, p. 29.) The **anhydrids** (see p. 65) are derived from acids by removal of water. Thus: $2HNO_3 - H_2O = N_2O_5$; $H_2SO_4 - H_2O = SO_3$; $2H_3PO_4 - 3H_2O = P_2O_5$.

**Composition and Constitution.**—The characters of a compound depend not only upon the kind and number of its atoms, but also upon the manner in which they are attached to each other. There are, for instance, two substances, each having the **empirical formula** $C_2H_4O_2$, one of which is a strong acid, the other a neutral ester. As the molecule of each contains the same number and kind of atoms, the differences in their properties must be due to differences in the manner in which the atoms are linked together.

**The composition of a compound is the number and kind of atoms contained in its molecule; and is shown by its empirical formula.**

**The constitution of a compound is the number and kind of atoms and their relations to each other, within its molecule; and is shown by its rational formula.**

**A rational formula** is one which partly or completely indicates the constitution of the body. Rational formulæ are either **typical** or **graphic.** In the system of **typical formulæ** all substances are considered as being so constituted that their rational formulæ may be referred to one of three classes or **types,** or to a combination of two of these types. These three classes, being named after the most common substance occurring in each, are expressed thus:

| The hydrogen type. | The Water type. | The ammonia type. |
|---|---|---|
| $\left.\begin{matrix}H\\H\end{matrix}\right\}$ | $\left.\begin{matrix}H\\H\end{matrix}\right\}O$ | $\left.\begin{matrix}H\\H\\H\end{matrix}\right\}N$ |
| $\left.\begin{matrix}H_2\\H_2\end{matrix}\right\}$ etc., | $\left.\begin{matrix}H_2\\H_2\end{matrix}\right\}O_2$ etc., | $\left.\begin{matrix}H_2\\H_2\\H_2\end{matrix}\right\}N_2$ etc., |

it being considered that the formula of any substance of known constitution can be indicated by substituting the proper element, or radical, for one or more of the atoms of the type, thus:

$\left.\begin{matrix}Cl\\H\end{matrix}\right\}$ Hydrochloric acid. $\left.\begin{matrix}(C_2H_5')\\H\end{matrix}\right\}O$ Alcohol. $\left.\begin{matrix}(C_2H_5)'\\H\\H\end{matrix}\right\}N$ Ethylamin. $\left.\begin{matrix}Cl_2\\Ca\end{matrix}\right\}$ Calcium chlorid. $\left.\begin{matrix}(SO_2)''\\H_2\end{matrix}\right\}O_2$ Sulfuric acid. $\left.\begin{matrix}(CO)''\\H_2\\H_2\end{matrix}\right\}N_2$ Urea.

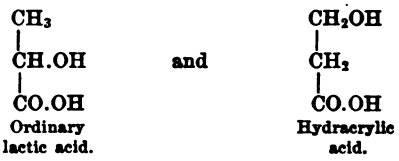
Typical formulæ are of great service in the classification of compound substances, as well as to indicate, to a certain degree, their nature and the method of the reactions into which they enter. Thus in the case of the two substances mentioned above, as both having the composition $C_2H_4O_2$, we find on examination that one contains the group $(CH_3)'$, while the other contains the group $(C_2H_3O)'$. The difference in their constitution at once becomes apparent in their typical formulæ, $\left.\begin{matrix}(CHO)'\\(CH_3)'\end{matrix}\right\}O$ and $\left.\begin{matrix}(C_2H_3O)'\\H\end{matrix}\right\}O$, indicating differences in their properties, which we find upon experiment to exist. The first substance is neutral in reaction and possesses no acid properties; it closely resembles a salt of an acid having the formula $\left.\begin{matrix}(CHO)\\H\end{matrix}\right\}O$. The second substance, on the other hand, has a strongly acid reaction, and markedly acid properties, as indicated by the oxidized radical and the extra-radical hydrogen. It is capable of forming salts by the substitution of an atom of a univalent, basylous element for its single replaceable atom of hydrogen: $\left.\begin{matrix}(C_2H_3O)'\\Na\end{matrix}\right\}O$.

Although typical formulæ have been and still are of great service, many cases arise, especially in treating of the more complex organic substances, in which they do not sufficiently indicate the relations between the atoms which constitute the molecule, and thus fail to convey a proper idea of the nature of the substance. Considering, for example, the ordinary lactic acid, we find its composition to be $C_3H_6O_3$, which, expressed typically, would be $\left.\begin{matrix}(C_3H_4O)''\\H_2\end{matrix}\right\}O_2$, a constitution supported by the fact that the radical $(C_3H_4O)''$ may be obtained in other compounds, as $\left.\begin{matrix}(C_3H_4O)''\\Cl_2\end{matrix}\right\}$. This constitution, however, cannot be the true one, because in the first place, lactic acid is not di-

basic, but monobasic; and in the second place, there is another acid, called hydracrylic acid, having an identical composition, yet differing in its products of decomposition. These differences in the properties of the two acids must be due to a different *arrangement* of atoms in their molecules, a view which is supported by the sources from which they are obtained and the nature of their products of decomposition.

To express the constitution of such bodies **graphic formulæ** are used, in which the position of each atom in relation to the others is set forth. The constitution of the two lactic acids would be expressed by graphic formulæ in this way:

or,




Ordinary lactic acid. Hydracrylic acid.

Graphic formulæ are usually still further abbreviated, bonds being indicated by dots; thus: $CH_3$. CHOH. COOH, and $CH_2OH$. $CH_2$. COOH.

It must be understood that these graphic formulæ are simply intended to show the relative attachments of the atoms, and are in nowise intended to convey the idea that the molecule is spread out upon a flat surface, with the atoms arranged as indicated in the diagram.

Great care and much labor are required in the construction of these graphic formulæ, the positions of the atoms being determined by a close study of the methods of formation, and of the products of decomposition of the substance under consideration. Naturally in a matter of this nature, there is always room for differences of opinion —indeed, the entire atomic theory is open to question, as is the theory of gravitation itself. But whatever may be advanced, two facts cannot be denied: first, that chemistry owes its advancement within the past half-century to the atomic theory, which to-day is more in consonance with observed facts than any substitute which can be offered; second, that without the use of graphic formulæ it is impossible to

offer any adequate explanation of the reactions which we observe in dealing with the more complex organic substances.

In chemistry, as in other sciences, a sharp distinction must always be made between facts and theories: the former, once observed, are immutable additions to our knowledge; the latter are of their nature subject to change with our increasing knowledge of facts. We have every reason for believing, however, that the supports upon which the atomic theory rests are such that, although it may be modified in its details, its essential features will remain unaltered.

**Classification of the Elements.**—Berzelius was the first to divide all the elements into two great classes, to which he gave the names **metals** and **metalloids.** The metals, being such substances as are opaque, possess what is known as metallic luster, are good conductors of heat and electricity, and are electro-positive; the metalloids, on the other hand, such as are gaseous, or, if solid, do not possess metallic luster, have a comparatively low power of conducting heat and electricity, and are electro-negative.

This division, based upon purely physical properties, which, in many cases, are ill-defined, has become insufficient. Several elements formerly classed under the above rules with the metals, resemble the metalloids in their chemical characters much more closely than they do any of the metals. Indeed, by the characters mentioned above, it is impossible to draw any line of demarcation which shall separate the elements distinctly into two groups.

The classification of the elements should be such that each group shall contain elements whose *chemical* properties are similar—the *physical* properties being considered only in so far as they are intimately connected with the chemical. The arrangement of elements into groups is not equally easy in all cases. Some groups, as the chlorin group, are sharply defined, while the members of others differ from each other more widely in their properties. The position of most of the more recently discovered elements is still uncertain, owing to the imperfect state of our knowledge of their properties.

The method of classification which we will adopt, and which we believe to be more natural than any hitherto suggested, is based upon the chemical properties of the oxids and upon the valence of the elements. We abandon the division into metals and metalloids, and substitute for it a division into four great classes, according to the nature of the oxids and the existence or non-existence of oxysalts. In the first of these classes hydrogen and oxygen are placed together, for the reason that, although they differ from each other in many of their properties, they together form the basis of our classification, and may, for this and other reasons, be regarded as typical

elements. They both play important parts in the formation of acids, and neither would find a suitable place in either of the other classes. Our primary division would then be as follows:

**Class I.—Typical elements.**

**Class II.—Elements whose oxids unite with water to form acids, never to form bases. Which do not form oxysalts.**

This class contains all the so-called metalloids except hydrogen and oxygen.

**Class III.—Elements whose oxids unite with water, some to form bases, others to form acids. Which form oxysalts.**

**Class IV.—Elements whose oxids unite with water to form bases; never to form acids. Which form oxysalts.**

In this class are included the more strongly electro-positive metals.

Within the classes a further subdivision is made into groups, each group containing those elements within the class which have equal valences, which form corresponding compounds, and whose *chemical characters* are otherwise similar.

For the sake of convenience the term **metal** is retained to apply to the members of Classes III and IV; the term **non-metal** being used for those belonging to Class II.

### Class I. Typical Elements.

GROUP I.—Hydrogen. GROUP II.—Oxygen.

### Class II. Acidulous Elements.

GROUP I.—Fluorin, chlorin, bromin, iodin.
GROUP II.—Sulfur, selenium, tellurium.
GROUP III.—Nitrogen, phosphorus, arsenic, antimony.
GROUP IV.—Boron.
GROUP V.—Carbon, silicon.
GROUP VI.—Vanadium, niobium, tantalium.
GROUP VII.—Molybdenum, tungsten, osmium.

### Class III. Amphoteric Elements.

GROUP I.—Gold.
GROUP II.—Chromium, manganese, iron.
GROUP III.—Uranium.
GROUP IV.—Lead.
GROUP V.—Bismuth.
GROUP VI.—Titanium, germanium, zirconium, tin.
GROUP VII.—Palladium, platinum.
GROUP VIII.—Rhodium, ruthenium, iridium.

### Class IV. Basylous Elements.

GROUP I.—Lithium, sodium, potassium, rubidium, cesium, silver.
GROUP II.—Thallium.
GROUP III.—Calcium, strontium, barium.
GROUP IV.—Magnesium, zinc, cadmium.
GROUP V.—Beryllium, aluminium, scandium, gallium, indium.
GROUP VI.—Nickel, cobalt.
GROUP VII.—Copper, mercury.
GROUP VIII.—Cerium, neodym, praseodym, erbium.
GROUP IX.—Yttrium, lanthanum, samarium, ytterbium.
GROUP X.—Thorium.

# INORGANIC CHEMISTRY.

## CLASS I.—TYPICAL ELEMENTS.

### HYDROGEN — OXYGEN.

ALTHOUGH, in a strict sense, hydrogen is regarded by most chemists as the one and only type-element — that whose atom is the unit of atomic and molecular weights — the important part which oxygen plays in the formation of those compounds whose nature forms the basis of our classification, its acid-forming power in organic compounds, and the differences existing between its properties and those of the elements of the sulfur group, with which it is usually classed, warrant us in separating it from the other elements and elevating it to the position it here occupies.

### HYDROGEN.

*Symbol*=H—*Univalent*—*Atomic weight*=1—*Molecular weight*=2—*Sp. gr.*=0.06926A*—*One litre weighs* 0.0896 *gram*†—100 *cubic inches weigh* 2.1496 *grains*‡—1 *gram measures* 11.16 *litres*†—1 *grain measures* 46.73 *cubic inches*‡—*Name derived from* ὕδωρ=*water, and* γεννάω=*I produce*—*Discovered by Cavendish in* 1766.

**Occurrence.**—Occurs free in volcanic gases, in fire-damp, occluded in meteorites, in the gases exhaled from the lungs, and in those of the stomach and intestine. In combination in water, hydrogen sulfid, ammoniacal compounds, and in many organic substances.

**Preparation.**—(1) By electrolysis of water, H is given off at the negative pole. Utilized when pure H is required.

(2) By the dissociation of water at very high temperatures.

(3) By the decomposition of water by certain metals. The alkali metals decompose water at the ordinary temperature:

| $Na_2$ | + | $2H_2O$ | = | $2NaHO$ | + | $H_2$ |
|---|---|---|---|---|---|---|
| Sodium. | | Water. | | Sodium hydroxid. | | Hydrogen. |

Some other metals. such as iron and copper, effect the decomposition only at high temperatures:

| $3Fe_2$ | + | $8H_2O$ | = | $2Fe_3O_4$ | + | $8H_2$ |
|---|---|---|---|---|---|---|
| Iron. | | Water. | | Triferric tetroxid. | | Hydrogen. |

*Air = 1. When the sp. gr. is referred to H = 1, A is replaced by H.
†At 0° C. and 760 mm. barometric pressure.
‡At 60° F. and 30 inches bar. pressure.

(4) By decomposition of water, passed over red-hot coke:

$$\underset{\text{Carbon.}}{C} + \underset{\text{Water.}}{2H_2O} = \underset{\text{Carbon dioxid.}}{CO_2} + \underset{\text{Hydrogen.}}{2H_2}$$

or at a higher temperature:

$$\underset{\text{Carbon.}}{C} + \underset{\text{Water.}}{H_2O} = \underset{\text{Carbon monoxid.}}{CO} + \underset{\text{Hydrogen.}}{H_2}$$

(5) By decomposition of mineral acids, in the presence of water, by zinc and certain other metals:

$$\underset{\text{Zinc.}}{Zn} + \underset{\text{Sulfuric acid.}}{H_2SO_4} + \underset{\text{Water.}}{xH_2O} = \underset{\text{Zinc sulfate.}}{ZnSO_4} + \underset{\text{Hydrogen.}}{H_2} + \underset{\text{Water.}}{xH_2O}$$

The water serves to dissolve the zinc sulfate. Chemically pure zinc, or zinc whose surface has been covered with an alloy of zinc and mercury, does not decompose the acid unless it forms part of a galvanic battery whose circuit is closed. The zincs of galvanic batteries are therefore covered with the alloy mentioned—are amalgamated—to prevent waste of zinc and acid.

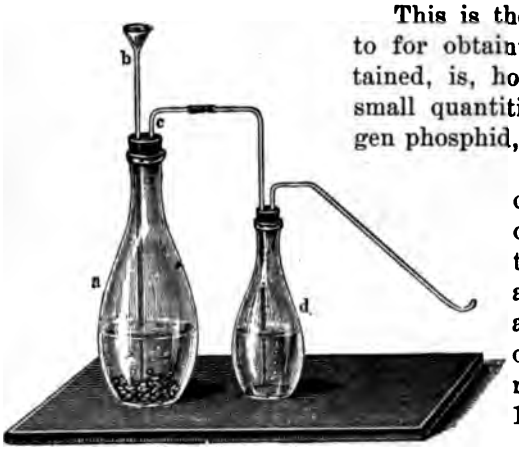



FIG. 18.

This is the method usually resorted to for obtaining H. The gas so obtained, is, however, contaminated with small quantities of other gases, hydrogen phosphid, sulfid and arsenid.

Hydrogen, carbon dioxid, hydrogen sulfid, and other gases produced by the action of a liquid upon a solid at ordinary temperatures, are best prepared in one of the forms of apparatus shown in Figs. 19, 19 and 20.

The solid material is placed in the larger bottle (Fig. 18), or, over a layer of broken glass about five centimetres thick, in the bottle *a* (Fig. 19). The liquid reagent is from time to time introduced by the funnel tube, Fig. 18; or the bottle *b*, Fig. 19, is filled with it. The wash-bottles are partially filled with water to arrest any liquid or solid impurity. The apparatus, Figs. 19 and 20, have the advantage of being always ready for use. When the stopcock is open the gas escapes. When it is closed the internal pressure depresses the level of the liquid in *a* into the layer of broken glass, and the action is arrested. Kipp's apparatus, Fig. 20, is another convenient form of constant apparatus. The solid reagent is placed in the central bulb.

(6) By heating together a mixture of zinc dust and dry-slacked lime:

$$\underset{\text{Zinc.}}{Zn} + \underset{\text{Calcium hydroxid.}}{CaH_2O_2} = \underset{\text{Zinc oxid.}}{ZnO} + \underset{\text{Calcic monoxid.}}{CaO} + \underset{\text{Hydrogen.}}{H_2}$$

**Properties.**—*Physical.*—Hydrogen is a colorless, odorless, tasteless gas; 14.47 times lighter than air, being the lightest substance known. The weight of a litre, 0.0896 gram, is called a crith (κριθή = barleycorn). From this the weight of a litre of any gas may be calculated by multiplying half its molecular weight by .0896. It is almost insoluble in water and alcohol. It conducts heat and electricity better than any other gas. In obedience to the law: **The diffusibility of two gases varies inversely as the square roots of their densities,** it is the most rapidly diffusible of gases. The rapidity with which this diffusion takes place renders the use of hydrogen, which has been kept for even a short time in gas-bags or gasometers, dangerous. It has been liquefied by a temperature of —240° (—400° F.) under a pressure of 13.3 atm. The liquid is clear and colorless, boils at —238° (396.4° F.), and has a sp. gr. of 0.068.

FIG. 19.

FIG. 20.

Certain metals have the power of absorbing large quantities of hydrogen, which is then said to be **occluded.** Palladium absorbs 980 volumes of the gas when used as the negative electrode in the electrolysis of water. The occluded gas is driven off by the application of heat, and possesses great chemical activity, similar to that which it has when in the nascent state. This latter quality, and the fact that heat is liberated during the occlusion, would seem to indicate that the gas is contained in the metal, not in a mere physical state of condensation, but in chemical combination.

*Chemical.*—Hydrogen exhibits no great tendency to combine with other elements at ordinary temperatures. It combines explosively,

however, with chlorin under the influence of sunlight, and with fluorin even in the dark. It does not support combustion, but, when ignited, burns with a pale blue and very hot flame; the result of the combination being water. Mixtures of hydrogen and oxygen explode violently on the approach of flame, or by the passage of the electric spark, the explosion being caused by the sudden expansion of the vapor of water formed, under the influence of the heat of the reaction. Hydrogen also unites with oxygen when brought in contact with spongy platinum. Many compounds containing oxygen give up that element when heated in an atmosphere of hydrogen:

| $CuO$ | + | $H_2$ | = | $Cu$ | + | $H_2O$ |
|---|---|---|---|---|---|---|
| Cupric oxid. | | Hydrogen. | | Copper. | | Water. |

**The removal of oxygen from a compound is called a reduction or deoxidation.** In a broader sense the term reduction is applied to **any diminution in the relative quantity of the electro-negative factor in a compound.** Thus mercuric chlorid, $HgCl_2$ (Hg 200: Cl 71) is *reduced* to mercurous chlorid, $Hg_2Cl_2$ (Hg 200: Cl 35.5).

At the instant that H is liberated from its compounds it has a deoxidizing power similar to that which ordinary H possesses only at elevated temperatures, and its tendency to combine with other elements is greater than under other conditions. The greater energy of H, and of other elements as well, in this **nascent state,** may be thus explained. Free H exists in the form of molecules, each one of which is composed of two atoms, but at the instant of its liberation from a compound, it is in the form of individual atoms, and that portion of force required to split up the molecule into atoms, necessary when free H enters into reaction, is not required when the gas is in the nascent state.

In its physical and chemical properties, this element more closely resembles those usually ranked as metals than it does those forming the class of non-metals, among which it is usually placed. Its conducting power, as well as its relation to the acids, which may be considered as salts of H, tend to separate it from the non-metals.

**Analytical Characters.**—(1) Burns with a faintly blue flame, which deposits water on a cold surface brought over it; (2) Mixed with oxygen, explodes on contact with flame, producing water.

## HELIUM.

A gaseous element existing in certain minerals and in many spring waters. Its atomic weight is 3.97. Its spectrum consists of a single bright yellow line coincident with $D_3$ of the solar spectrum. It has been liquefied.

## OXYGEN.

*Symbol* = O — *Bivalent* — *Atomic weight* = 15.87; *molecular weight* = 31.74 — *Sp. gr.* = 1.10563 A (*calculated* = 1.1088); 15.95 H; *sp. gr. of liquid*=0.9787 — *One litre weighs* 1.422 *grams;* 100 *cubic inches weigh* 34.27 *grains* — *Name derived from* ὀξύς = *acid, and* γεννάω = *I produce* — *Discovered by Mayow in* 1674; *rediscovered by Priestley in* 1774.

**Occurrence.**— Oxygen is the most abundant of the elements. It exists free in atmospheric air; in combination in a great number of substances, mineral, vegetable, and animal.

**Preparation.**— (1) By heating certain oxids:

$$\underset{\text{Mercuric oxid.}}{2HgO} = \underset{\text{Mercury.}}{2Hg} + \underset{\text{Oxygen.}}{O_2}$$

This was the method used by Priestley. 100 grams of mercuric oxid produce 5.16 litres of oxygen:

$$\underset{\text{Manganese dioxid.}}{3MnO_2} = \underset{\text{Trimanganic tetroxid.}}{Mn_3O_4} + \underset{\text{Oxygen.}}{O_2}$$

The black oxid of manganese is heated to redness in an iron or clay retort (Scheele, 1775); and 100 grams yield 8.51 litres of oxygen.

(2) By the electrolysis of water, acidulated with sulfuric acid, O is given off at the positive pole.

(3) By the action of sulfuric acid upon certain compounds rich in O: manganese dioxid, potassium dichromate, and plumbic peroxid:

$$\underset{\text{Manganese dioxid.}}{2MnO_2} + \underset{\text{Sulfuric acid.}}{2H_2SO_4} = \underset{\text{Manganous sulfate.}}{2MnSO_4} + \underset{\text{Water.}}{2H_2O} + \underset{\text{Oxygen.}}{O_2}$$

100 grams of manganese dioxid produce 12.83 litres of O.

(4.) By decomposing $H_2SO_4$ at a red heat, $2H_2SO_4 = 2SO_2 + 2H_2O + O_2$.

(5) By the decomposition by heat of certain salts rich in O: alkaline permanganates, nitrates, and chlorates.

The best method, and that usually adopted, is by heating a mixture of potassium chlorate and manganese dioxid in equal parts, moderately at first and more strongly toward the end of the reaction. The chlorate gives up all its O (27.33 litres from 100 grams of the salt), according to the equation:

$$\underset{\text{Potassium chlorate.}}{2KClO_3} = \underset{\text{Potassium chlorid.}}{2KCl} + \underset{\text{Oxygen.}}{3O_2}$$

At the end of the operation the manganese dioxid remains, apparently unchanged.

A small quantity of free chlorin usually exists in the gas pro-

duced by this reaction. If the oxygen is to be used for inhalation, the chlorin should be removed by allowing the gas to stand over water for 24 hours.

When heat is required for the generation of gases the operation is conducted in retorts of glass or metal, or in the apparatus shown in Fig. 21. If the gas be collected over water the disengagement tube

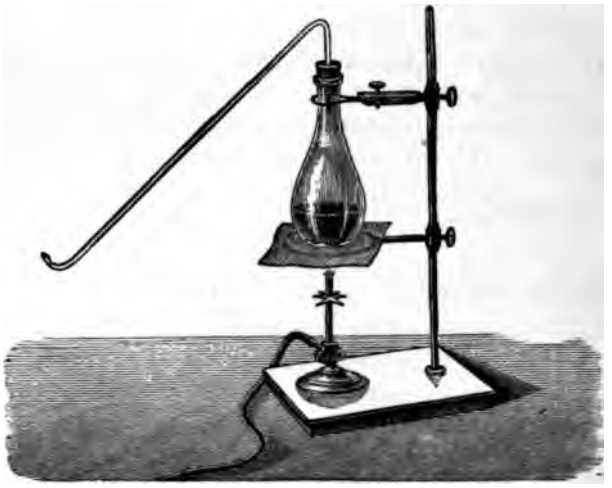


FIG. 21.

must be withdrawn from the water, before the source or heat is removed. Neglect of this precaution will cause an explosion, by the the entrance of water into the hot flask, by the contraction of the gas contained in it, on partial cooling.

(6) By the action of water upon sodium peroxid:

| $2Na_2O_2$ | + | $2H_2O$ | = | $4NaHO$ | + | $O_2$ |
|---|---|---|---|---|---|---|
| Sodium peroxid. | | Water. | | Sodium hydroxid. | | Oxygen. |

(7) By the mutual decomposition of potassium permanganate and hydrogen peroxid, in the presence of sulfuric acid:

| $H_2O_2$ | + | $K_2Mn_2O_8$ | + | $3H_2SO_4$ | = | $K_2SO_4$ |
|---|---|---|---|---|---|---|
| Hydrogen peroxid. | | Potassium permanganate. | | Sulfuric acid. | | Potassium sulfate. |

| + | $2MnSO_4$ | + | $4H_2O$ | + | $3O_2$ |
|---|---|---|---|---|---|
| | Manganous sulfate. | | Water. | | Oxygen. |

One kilo $H_2O_2$ (3 per cent) and 500 cc. dilute $H_2SO_4$ (1:5) are placed in the generating flask and 56 grams $K_2Mn_2O_8$, dissolved in $H_2O$, are gradually added. With these quantities 20 litres O are obtained.

(8) By the action of dilute hydrochloric acid upon a mixture of 2

parts barium peroxid, 1 part manganese dioxid, and 1 part plaster of Paris, compressed into cubes about 1½ cent. square.

Methods 6, 7, and 8 have the advantage that heat is not required, and the forms of apparatus, Figs. 18, 19, and 20, may be used.

**Properties.**—*Physical.*—Oxygen is a colorless, odorless, tasteless gas, soluble in water in the proportion of 7.08 cc. in 1 litre of water at 14.8° (58.6° F.), somewhat more soluble in absolute alcohol. It liquefies at —140° (—220° F.) under a pressure of 300 atmospheres. Liquid oxygen boils at —187.4° (—294.5° F.) at the ordinary pressure. The sp. gr. of liquid oxygen is 0.9787.

*Chemical.*— Oxygen is characterized, chemically, by the strong tendency which it exhibits to enter into combination with other elements. It forms binary compounds with all elements except fluorin and bromin. With most elements it unites directly, especially at elevated temperatures. In many instances this union is attended by the appearance of light, and always by the extrication of heat. The luminous union of O with another element constitutes the familiar phenomenon of **combustion**, and is the principal source from which we obtain so-called artificial heat and light. A body is said to be **combustible** when it is capable of so energetically combining with the oxygen of the air as to liberate light as well as heat. Gases are said to be **supporters of combustion**, when combustible substances will unite with them, or with some of their constituents, the union being attended with the appearance of heat and light. The distinction between combustible substances and supporters of combustion is, however, one of mere convenience. The action taking place between the two substances, one is as much a party to it as the other. A jet of air burns in an atmosphere of coal-gas as readily as a jet of coal-gas burns in air.

**An oxidation is a chemical action in which oxygen combines with an element or a compound.** The burning of coal: $C+O=CO$ or $C+O_2=CO_2$; and the formation of acetic acid from alcohol: $C_2H_6O+O_2=C_2H_4O_2+H_2O$, are oxidations. In a broader sense the word "oxidation" is sometimes used as the opposite to "reduction" (p. 62) to apply to any increase in the relative quantity of the electronegative element in a compound. Thus the conversion of $FeCl_2$ (Fe 112:Cl 142) into $Fe_2Cl_6$ (Fe 112:Cl 213) may be referred to as an oxidation, although it is, more properly, a chlorination.

The compounds of oxygen—the **oxids**—are divisible into three groups:

1. **Anhydrids.**—Oxids capable of combining with water to form *acids*. Thus *sulfuric anhydrid*, $SO_3$, unites with water to form *sulfuric acid*, $H_2SO_4$.

The term anhydrid is not limited in application to *binary* com-

pounds, but applies to any substance capable of combining with water to form an acid. Thus the compound $C_4H_6O_3$ is known as acetic anhydrid, because it combines with water to form acetic acid: $C_4H_6O_3 + H_2O = 2C_2H_4O_2$. (See compounds of arsenic and sulfur.)

2. **Basic oxids** are such as combine with water to form bases. Thus calcium oxid, CaO, unites with water to form calcium hydroxid, $CaH_2O_2$.

3. **Saline, neutral or indifferent oxids** are such as are neither acid nor basic in character. In some instances they are essentially neutral, as in the case of the protoxid of hydrogen, or water. In other cases they are formed by the union of two other oxids, one basic, the other acid in quality, such as the red oxid of lead, $Pb_3O_4$, formed by the union of a molecule of the acidulous peroxid, $PbO_2$, with two of the basic protoxid, PbO. It is to oxids of this character that the term "saline" properly applies.

The process of respiration is very similar to combustion, and as oxygen gas is the best supporter of combustion, so, in the diluted form in which it exists in atmospheric air, it is not only the best, but the only supporter of animal respiration. (See Carbon dioxid.)

**Analytical Characters.**— 1. A glowing match-stick bursts into flame in free oxygen. 2. Free O, when mixed with nitrogen dioxid, produces a brown gas.

**Ozone.**—*Allotropic oxygen.*—Air through which discharges of static electricity have been passed, and oxygen obtained by the decomposition of water (if electrodes of gold or platinum be used), have a peculiar odor, somewhat resembling that of sulfur, which is due to the conversion of a part of the oxygen into ozone.

Ozone is produced: 1. By the decomposition of water by the battery. 2. By the slow oxidation of phosphorus in damp air. 3. By the action of concentrated sulfuric acid upon barium dioxid. 4. By the passage of silent electric discharges through air or oxygen.

In the preparation of ozonized oxygen the best results are obtained by passing a slow current of oxygen through an apparatus made entirely of glass and platinum, cooled by a current of cold water, and traversed by the invisible discharge of an induction coil.

Pure, liquid ozone has been obtained by subjecting ozonized oxygen to the temperature of liquid oxygen at the atmospheric pressure. It is a dark blue liquid, almost opaque in layers 2 mm. thick, which is not decomposed at the ordinary temperature, but converted into a bluish gas. It boils at —119° (—182.2°F.).

When oxygen is ozonized it contracts slightly in volume, and when the ozone is removed from ozonized oxygen by mercury or potassium iodid the volume of the gas is not diminished. These facts, and the great chemical activity of ozone, have led chemists

to regard it as condensed oxygen; the molecule of ozone being represented thus (OOO), while that of ordinary oxygen is (OO).

Ozone is very sparingly soluble in water, more soluble in the pressure of hypophosphites, insoluble in solutions of acids and alkalies. In the presence of moisture it is slowly converted into oxygen at 100° (212° F.), a change which takes place rapidly and completely at 237° (459° F.) It is a powerful oxidant; it decomposes solutions of potassium iodid with formation of potassium hydroxid, and liberation of iodin; it oxidizes all metals except gold and platinum, in the presence of moisture; it decolorizes indigo and other organic pigments, and acts rapidly upon rubber, cork, and other organic substances.

**Analytical Characters.**—1. Neutral litmus paper, impregnated with solution of potassium iodid, is turned blue when exposed to air containing ozone. The same litmus paper without iodid is not affected. 2. Manganous sulfate solution is turned brown by ozone. 3. Solutions of thallous salts are colored yellow or brown by ozone. 4. Paper impregnated with fresh tincture of natural (unpurified) guaiacum is colored blue by ozone. 5. Paper impregnated with solution of manganous sulfate, or lead hydroxid, or palladium chlorid is colored dark brown or black by ozone. 6. Metallic silver is blackened by ozone.

When inhaled, air containing 0.07 gram of ozone per litre causes intense coryza and hæmoptysis. It is probable that ozone is by no means as constant a constituent of the atmosphere as was formerly supposed. (See Hydrogen dioxid.)

## COMPOUNDS OF HYDROGEN AND OXYGEN.

Two are known—hydrogen oxid or water, $H_2O$; hydrogen peroxid or oxygenated water, $H_2O_2$.

## WATER.

$H_2O$—*Molecular weight*=18 *Sp. gr.*=1—*Vapor density*=0.6218 A; *calculated*=0.6234—*Composition discovered by Priestley in* 1780—1 *cc. weighs* 1 *gm. at* 4° *and* 0.999 *gm. at* 16°—1 *cubic inch weighs* 252.6 *grains at* 60° *F.*

**Occurrence.**—In unorganized nature $H_2O$ exists in the gaseous form in atmospheric air and in volcanic gases; in the liquid form very abundantly; and as a solid in snow, ice, and hail.

**As water of crystallization** it exists in definite proportions in certain crystals, to the maintenance of whose shape it is necessary.

In the organized world $H_2O$ forms a constituent part of every tissue and fluid.

**Formation.**—Water is formed: 1. By union, brought about by elevation of temperature, of one vol. O with two vols. H.

2. By burning H, or substances containing it, in air or in O.

3. By heating organic substances containing H to redness with cupric oxid, or with other substances capable of yielding O. This method of formation is utilized to determine the amount of H contained in organic substances.

4. When an acid and a hydroxid react upon each other to form a salt:

| $H_2SO_4$ | + | $2KHO$ | = | $K_2SO_4$ | + | $2H_2O$ |
|---|---|---|---|---|---|---|
| Sulfuric acid. | | Potassium hydroxid. | | Potassium sulfate. | | Water. |

5. When a metallic oxid is reduced by hydrogen:

| $CuO$ | + | $H_2$ | = | $Cu$ | + | $H_2O$ |
|---|---|---|---|---|---|---|
| Cupric oxid. | | Hydrogen. | | Copper. | | Water. |

6. In the reduction and oxidation of many organic substances.

Pure $H_2O$ is not found in nature. When required free from ordinary impurities it is separated from suspended matters by filtration, and from dissolved substances by distillation.

**Properties.**—*Physical.*—With a barometric pressure of 760 mm. $H_2O$ is solid below 0° (32° F.); liquid between 0° (32° F.) and 100° (212° F.); and gaseous above 100° (212° F.). When $H_2O$ is enclosed in capillary tubes, or is at complete rest, it may be cooled to —15° (5° F.) without solidifying. If, while at this temperature, it be agitated, it solidifies instantly, and the temperature suddenly rises to 0° (32° F.). The melting-point of ice is lowered 0.0075° (0.0135° F.) for each additional atmosphere of pressure.

The boiling-point is subject to greater variations than the freezing-point. It is the lower as the pressure is diminished, and the higher as it is increased. Advantage is taken of the reduced boiling-point of solutions in vacuo for the separation of substances, such as cane sugar, which are injured at the temperature of boiling $H_2O$. On the other hand, the increased temperature that may be imparted to liquid $H_2O$ under pressure is utilized in many processes in the laboratory and in the arts, for effecting solutions and chemical actions which do not take place at lower temperatures. The boiling-point of $H_2O$ holding solid matter in solution is higher than that of pure $H_2O$, the degree of increase depending upon the amount and nature of the substance dissolved. On the other hand, mixtures of $H_2O$ with liquids of lower boiling-point boil at temperatures less than 100° (212° F.). Although the conversion of water into water-vapor takes place most actively at 100° (212° F.), water and ice evaporate at all temperatures.

Water is the best solvent we have, and acts in some instances as a simple solvent, in others as a chemical solvent.

Vapor of water is colorless, transparent, and invisible. Sp. gr. 0.6234 A or 9 H. A litre of vapor of water weighs 0.8064. The latent heat of vaporization of water is 536.5; that is, as much heat is required to vaporize 1 kilo. of water at 100° as would suffice to raise 536.5 kilos. of water 1° in temperature. In passing from the liquid to the gaseous state, water expands 1,696 times in volume.

*Chemical.*—Water may be shown to consist of 1 vol. O and 2 vols. H, or 8 by weight of O and 1 by weight of H, either by analysis or synthesis.

**Analysis is the reducing of a compound to its constituent parts or elements.**

**Synthesis is the formation of a compound from its elements.** A partial synthesis is one in which a complex compound is produced from a simpler one, but not from the elements.

Water may be resolved into its constituent gases: 1. By electrolysis of acidulated water; H being given off at the negative and O at the positive pole. 2. By passing vapor of $H_2O$ through a platinum tube heated to whiteness, or through a porcelain tube heated to about 1,100°. The decomposition of a compound gas or vapor by elevation of temperature is called **dissociation.** 3. By the action of the alkali metals. Hydrogen is given off, and the metallic hydroxid remains in solution in an excess of $H_2O$. 4. By passing vapor of $H_2O$ over red-hot iron. Oxid of iron remains and H is given off.

Water combines with oxids to form new compounds, some of which are acids and others bases, known as **hydroxids.**

**A hydroxid is a compound formed by the replacement of half of the hydrogen of water by another element or by a radical.**

**A hydrate is a compound containing chemically combined water.** The act of union of a substance with water is referred to as **hydration.**

The hydroxids of the electro-negative elements and radicals are **acids**; most of those of the electro-positive elements and radicals are **basic hydroxids.**

Certain substances, in crystallizing, combine with a definite proportion of water, which is known as **water of crystallization,** and whose presence, although necessary to the maintenance of certain physical characters, such as color and crystalline form, does not modify their chemical reactions. In many instances a portion of the water of crystallization may be driven off at a comparatively low temperature, while a higher temperature is required to expel the remainder. This latter is known as **water of constitution.**

The symbol Aq (Latin, *aqua*) is frequently used to designate the water of crystallization, the water of constitution being indicated by $H_2O$. Thus $MgSO_4$, $H_2O+6Aq$ represents magnesium sulfate with one molecule of water of constitution and six molecules of water of crystallization. We consider it preferable, however, as the distinction between water of crystallization and water of constitution in many salts is only one of degree and not of kind, to use the symbol Aq to designate the sum of the two; thus, $MgSO_4+7Aq$.

Water decomposes the chlorids of the second class of elements (those of carbon only at high temperatures and under pressure). Thus phosphorous trichlorid forms phosphorous and hydrochloric acids: $PCl_3 + 3H_2O = H_3PO_3 + 3HCl$. A decomposition attended with absorption of water is called **hydrolysis.**

**Natural Waters.**—Natural waters which appear to the senses to be fit for drinking are called **potable waters,** in contradistinction to such as are, from their taste and appearance, obviously unfit for that use.

Potable waters may be classified, according to their origin, into four groups:

**Meteoric waters:** rain water and melted snow. These are the purest natural waters if uncontaminated; they contain very small quantities of solids, and are highly aerated. Rain water falling during the first part of a shower is less pure than that which falls subsequently. In districts where notable quantities of coal which contains sulfur are burnt, rain water contains more sulfates, ammoniacal salts, nitrates and nitrites than elsewhere.

**Surface waters:** the waters of rivers, lakes and ponds. These are mixtures, in varying proportions, of rain water, spring water and the drainage of the surrounding land. They vary greatly in natural purity, and are frequently contaminated by sewage and other refuse.

**Ground waters:** water which permeates the superficial stratum above the uppermost impermeable rock. This is the water obtained in surface wells and in driven wells. Its quality depends upon what is in and on the stratum in which the well is dug; a driven well in a sandy stratum remote from habitations yields an excellent water, while the water of a well near a privy vault or a defective sewer is more or less diluted sewage. In limestone districts ground water is hard.

**Deep waters:** spring waters and those of artesian wells.

*Spring water* is rain water which, having percolated through a portion of the earth's crust (in which it may also have been subjected to pressure), has become charged with solid and gaseous matter, varying in kind and quantity according to the nature of the strata

through which it has percolated, the duration of contact, and the pressure to which it was subject during such contact.

Spring waters from igneous rocks and from the older sedimentary formations are fresh and sweet, and any spring water may be considered such whose temperature is less than 20° (68° F.), and which does not contain more than 40 parts in 100,000 of solid matter; provided that a large proportion of the solid matter does not consist of salts having a medicinal action, and that sulfurous gases and sulfids are absent.

Artesian wells are artificial springs, produced by boring in a low-lying district, until a pervious layer, between two impervious strata, is reached; the outcrop of the system being in an adjacent elevated region.

**Impurities in Potable Waters.**—A water to be fit for drinking purposes should be cool, limpid and odorless; it should have an agreeable taste, neither flat, salty, nor sweetish, and it should dissolve soap readily, without formation of any flocculent precipitate. But, while it is safe to condemn a water which does not possess the above characters, it is by no means safe to regard all waters which do possess them as beyond suspicion. The most dangerous of all contaminations of drinking waters is by admixture of sewage, which may be present in a water in quantity sufficient to render it unfit for use and the water yet retain all of the characters of a good water above referred to. To determine whether a water is really fit for drinking a chemical analysis is necessary, and a bacteriological examination is desirable. For the methods of chemical analysis the student is referred to treatises on that subject. The constituents usually determined, and the interpretation of the results, are as follows:

**Total Solids.**—The amount of solid material dissolved in potable waters varies from 4.3 to 50 in 100,000 (2.5 to 29.2 grains per U. S. gal.); and a water containing more than the latter quantity is to be condemned on that account alone.

**Chlorids.**—The presence of the chlorids of the alkaline metals, in quantities not sufficient to be detectable by the taste, is of no importance *per se;* but in connection with the presence of organic impurity, a determination of the amount of chlorin affords a ready method of indicating the probable source of the organic contamination. As vegetable organic matter brings with it but small quantities of chlorids, while animal contaminations are rich in those compounds, the presence of a large amount of chlorin serves to indicate that organic impurity is of animal origin. Indeed, when time presses, as during an epidemic, it is best to rely upon determinations of chlorin, and condemn all waters containing more than 1.7 in 100,000 (1 grain per U. S. gal.) of that element.

**Hardness.**—The greater part of the solid matter dissolved in natural fresh waters consists of the salts of calcium, accompanied by less quantities of the salts of magnesium. The calcium salt is usually the bicarbonate or the sulfate; sometimes the chlorid, phosphate, or nitrate.

A water containing an excess of calcareous salt is said to be **hard**, and one not so charged is said to be **soft**. If the hardness be due to the presence of the bicarbonate it is **temporary**, if due to the sulfate it is **permanent**. Calcium carbonate is almost insoluble in pure water, but in the presence of free carbonic acid the more soluble bicarbonate is dissolved. But, on the water being boiled, it is decomposed, with precipitation of the carbonate. As calcium sulfate is held in solution by virtue of its own, albeit sparing, solubility, it is not deposited when the water is boiled.

The hardness is now usually reported in terms of calcium carbonate, $CaCO_3$, either in grains per gallon or parts in 100,000. It is also sometimes reported in "degrees," which represent grains of $CaCO_3$ per imperial gallon. Very soft waters contain about $5CaCO_3$ in 100,000, and hard waters 15 or over. Usually a water containing more than $20CaCO_3$ in 100,000 is considered too hard for domestic use, unless softened by boiling. But a water is not to be condemned solely because its hardness exceeds this limit, because in certain limestone districts all waters are very hard.

Waters which owe their hardness to excess of magnesium salts, cause intestinal disturbances in those not habituated to them.

**Organic Matter.**—Technically, organic impurities in a water consist of vegetable or animal matters containing nitrogen. We have seen that the quantity of chlorin affords an indication as to whether the organic impurity found to be present is of vegetable or of animal origin. Animal organic contamination has its origin in sewage, and its presence consequently indicates that the water is, or may at any moment become, the means of transmitting water-borne diseases, such as typhoid and cholera.

The nitrogenous substances in feces and urine consist of albuminous bodies, crystalline organic compounds (such as urea, leucin, etc.) and ammoniacal salts. By the action of micro-organisms, which exist in the soil and in water, the albuminous and crystalline compounds are gradually converted into ammonium compounds, which are subsequently oxidized by atmospheric or dissolved oxygen, aided by bacterial influence, to nitrites and later to nitrates. Consequently the amount of sewage contamination, and the degree in which such contamination has been subsequently modified, can be inferred from quantitative determinations of the nitrogen present in the several forms referred to.

In the usual process of water analysis the following factors are determined quantitatively:

A. Albuminoid ammonia, which represents the nitrogen present in albuminous and crystalline combination.

B. Free ammonia, which represents the ammoniacal compounds.

C. Nitrogen in nitrates and nitrites, and D. Nitrites.

If a water yield no albuminoid ammonia it is organically pure, even if it contain much free ammonia and chlorids. If it contain from .02 to .05 milligrams per litre (.002 to .005 in 100,000) it is still quite pure. When the albuminoid ammonia reaches 0.1 milligr. per litre (.01 in 100,000) the water is to be looked upon with suspicion; and it is to be condemned when the proportion reaches 0.15 (.015 in 100,000). When free ammonia is also present in considerable quantity, a water yielding 0.05 (.005 in 100,000) of albuminoid ammonia is to be looked upon with suspicion.

Nitrates and nitrites are present in rain water in quantities less than 0.5 parts in 100,000, calculated as nitrogen. When the amount exceeds this, these salts are considered as indicating previous contamination by organic matter which has been oxidized and whose nitrogen has been to some extent converted into nitrites and nitrates.

The quantity of nitrites in good waters does not exceed .002 in 100,000 when they are present. A larger quantity is considered as indicating previous organic contamination.

In some processes it is sought to measure the organic contamination by the amount of oxygen consumed in their oxidation by potassium permanganate. As these results take no account of other oxidations which may take place they are not reliable.

**Poisonous Metals.** — Natural waters containing notable quantities of iron compounds belong to the class of chalybeate mineral waters. Contact with metallic iron does not contaminate water. In districts where copper deposits exist the waters sometimes contain copper, and the waters of some streams contain arsenic.

Lead in drinking water has been a prolific source of chronic lead poisoning. As lead is only dissolved by water after oxidation, conditions favoring oxidation of the metal favor its solution. Such conditions are: the presence of nitrates, a highly aërated condition of the water, alternate wetting and drying of the surface of the metal, the absence of sulfates and carbonates, and the presence of much carbonic acid dissolved under pressure (soda water). Sulfates and carbonates prevent solution by the formation of a protecting coating of an insoluble salt. As a rule, the purer the water the more liable it is to dissolve lead when brought in contact with that metal, especially if the contact occur when the water is at a high temperature, or when it lasts for a long period.

**Bacteriological Examination of Water.**—In recent years much attention has been given to the examination of natural waters by bacteriological methods, plate cultures on gelatin, cultures in blood serum and on potatoes, and experiments on animals. Although in some instances pathogenic bacteria have been found in water, and although in the future valuable results will probably be obtained by these methods, the chief reliance in determining the quality of a drinking-water is still to be placed upon the older chemical processes.

**Purification of Water.**—The artificial means of rendering a more or less contaminated water fit for use are of five kinds: Distillation, subsidence, filtration, precipitation, and boiling.

Distillation is resorted to in the laboratory to obtain very pure water, also, on a larger scale, to purify drinking water. When distilled water is to be used for drinking it should be aërated and charged with salts to the extent of about 0.03 gram each of calcium bicarbonate and sodium chlorid to the litre.

In filtration suspended impurities are removed more or less completely by passing the water through a porous material. In *filter beds*, used to filter large quantities of water, sand is the filtering material used, either alone or combined with charcoal or spongy iron. In domestic filters, treating small quantities of water, the filtering material is quartz sand, charcoal, porous stone, or unglazed earthenware or porcelain. Whatever may be the size or construction of the filter, it must be cleaned periodically. If this be neglected the filter ceases to purify the water, and becomes itself a source of contamination. The usual method of cleaning is by reversing the current through the filter until the washings come away clear. Dissolved organic matter is in part removed by oxidation in filtration through sand filter beds several feet in thickness, or through much thinner layers of charcoal or porous iron. Typhoid and cholera germs pass, although in greatly diminished numbers, through all filters except those made of unglazed porcelain.

Precipitation methods were formerly used only to soften temporarily hard waters. One method consists in the addition of lime water in quantity just sufficient to convert the soluble calcium bicarbonate present into the insoluble carbonate. At present precipitation methods are also used, in combination with subsidence and filtration, to remove organic impurities; alum or a ferric salt is added, an excess being avoided, to form a gelatinous precipitate which carries the impurities down with it mechanically as it settles when the water is left at rest in the subsidence tanks; the water is drawn off from above the deposit to the filters, after a proper interval. Precipitation and subsidence are thus used to diminish the work required of the filters.

The purification of water by boiling can only be carried on on a small scale. It is very useful, however, to soften temporarily hard waters and, particularly, to sterilize infected waters. For the latter purpose the boiling must be continued actively for at least twenty minutes in a vessel closed except for a steam outlet, which is to be stopped with a plug of cotton when the vessel is taken off to cool.

**Natural Purification of Water.** — The water of brooks, rivers, and lakes which have been contaminated by sewage and other organic impurity becomes gradually purified by natural processes. Suspended particles are deposited upon the bottom and sides of the stream, more or less rapidly, according to their gravity and the rapidity of the current. The bicarbonates of calcium, magnesium, and iron gradually lose carbon dioxid, and are precipitated as carbonates, which mechanically carry down dissolved as well as suspended impurities. The decompositions, oxidations, and reductions to which organic matters are subject under the influence of atmospheric and dissolved oxygen and bacterial action bring about their gradual mineralization by conversion into ammonia and then into nitrates. The processes of nutrition of aquatic plant life absorb dissolved organic impurity, as well as the products of decomposition of nitrogenized substances. This natural purification proceeds the more rapidly the more contact with air is favored.

**Mineral Waters.**—Under this head are classed all waters which are of therapeutic or industrial value, by reason of the quantity or nature of the dissolved solids which they contain; or which have a temperature greater than 20° (68° F.).

The composition of mineral waters varies greatly, according to the nature of the strata or veins through which the water passes, and to the conditions of pressure and previous composition under which it is in contact with these deposits.

Although a sharply defined classification of mineral waters is not possible, one which is useful, if not accurate, may be made, based upon the predominance of some constituent, or constituents, which impart to the water a well-defined therapeutic value. A classification which has been generally adopted includes five classes:

I. *Acidulous waters;* whose value depends upon dissolved carbonic acid. They contain but small quantities of solids, principally the bicarbonates of sodium and calcium and sodium chlorid.

II. *Alkaline waters;* which contain quantities of the bicarbonates of sodium, potassium, lithium, and calcium, sufficient to communicate to them an alkaline reaction, and frequently a soapy taste; either naturally, or after expulsion of carbon dioxid by boiling.

III. *Chalybeate waters;* which contain salts of iron in greater proportion than 4 parts in 100,000. They contain ferrous bicar-

bonate, sulfate, crenate, and apocrenate, calcium carbonate, sulfates of potassium, sodium, calcium, magnesium, and aluminium, notable quantities of sodium chlorid, and frequently small amounts of arsenic. They have the taste of iron and are usually clear as they emerge from the earth. Those containing ferrous bicarbonate deposit a sediment on standing, by loss of carbon dioxid, and formation of ferrous carbonate.

IV. *Saline waters;* which contain neutral salts in considerable quantity. The nature of the salts which they contain is so diverse that the group may well be subdivided:

α. *Chlorin waters;* which contain large quantities of sodium chlorid, accompanied by less amounts of the chlorids of potassium, calcium, and magnesium. Some are so rich in sodium chlorid that they are not of service as therapeutic agents, but are evaporated to yield a more or less pure salt. Any natural water containing more than 300 parts in 100,000 of sodium chlorid belongs to this class, provided it do not contain substances more active in their medicinal action in such proportion as to warrant its classification elsewhere. Waters containing more than 1,500 parts in 100,000 are too concentrated for internal administration.

β. *Sulfate waters* are actively purgative from the presence of considerable proportions of the sulfates of sodium, calcium, and magnesium. Some contain large quantities of sodium sulfate, with mere traces of the calcium and magnesium salts, while in others the proportion of the sulfates of magnesium and calcium is as high as 3,000 parts in 100,000 to 2,000 parts in 100,000 of sodium sulfate. They vary much in concentration; from 500 to nearly 6,000 parts of total solids in 100,000. They have a salty, bitter taste, and vary much in temperature.

γ. *Bromin and iodin waters* are such as contain the bromids or iodids of potassium, sodium, or magnesium in sufficient quantity to communicate to them the medicinal properties of those salts.

V. *Sulfurous waters;* which hold hydrogen sulfid or metallic sulfids in solution. They have a disagreeable odor and are usually warm. They contain 20 to 400 parts in 100,000 of total solids.

**Physiological.**— Water is taken into the body both as a liquid and as a constituent of every article of food; the amount ingested by a healthy adult being 2.25 to 2.75 litres (2⅓ to 3 quarts) per diem. The greater the elimination and the drier the nature of the food the greater is the amount of $H_2O$ taken in the liquid form.

Water is a constituent of every tissue and fluid of the body, varying from 0.2 per cent. in the enamel of the teeth to 99.5 per cent. in the perspiration and saliva. It constitutes about 60 per cent. of the weight of the body.

The consistency of the various parts does not depend entirely upon the relative proportion of solids and $H_2O$, but is influenced by the nature of the solids. The blood, although liquid in the ordinary sense of the term, contains a less proportional amount of $H_2O$ than does the tissue of the kidneys, and about the same proportion as the tissue of the heart. Although the bile and mucus are not as fluid as the blood, they contain a larger proportion of $H_2O$ to solids than does that liquid.

Water is discharged by the kidneys, intestines, skin, and pulmonary surfaces. The quantity discharged is greater than that ingested; the excess being formed in the body by the oxidation of the H of its organic constituents.

## HYDROGEN DIOXID.

### HYDROGEN PEROXID—OXYGENATED WATER.

$H_2O_2$ — *Molecular weight* = 34—*Sp. gr.* = 1.455 — *Discovered by Thénard in* 1818.

Exists naturally in very minute quantity in rain-water, in air, and in the saliva.

This substance may be obtained in a state of purity by accurately following the process of Thénard. It may also be obtained, mixed with a large quantity of $H_2O$, by the action of dilute mineral acids on barium peroxid: $BaO_2+H_2SO_4 = BaSO_4 + H_2O_2$. It is also formed in small quantity during the slow oxidation of many elements and compounds, such as P, Pb, Zn, Cd, Al, alcohol, ether and the essences.

It is prepared industrially of 10–12 volume strength by gradually adding barium peroxid to dilute hydrofluoric acid solution, the mixture being maintained at a low temperature and constantly agitated; or, in still greater concentration by the action of dilute acids on sodium peroxid, care being had to prevent heating of the mixture: $Na_2O_2 + 2HCl = 2NaCl + H_2O_2$. Hydrogen peroxid is also formed when sodium peroxid is dissolved in water: $Na_2O_2 + 2H_2O = 2NaHO + H_2O_2$.

The pure substance is a colorless, syrupy liquid, which, when poured into $H_2O$, sinks under it before mixing. It has a disagreeable metallic taste, somewhat resembling that of tartar emetic. When taken into the mouth it produces a tingling sensation, increases the flow of saliva, and bleaches the tissues with which it comes in contact. It is still liquid at —30° (—22° F.). It is very unstable, and, even in darkness and at ordinary temperature, is gradually decomposed. At 20° (68° F.) the decomposition takes place more quickly and at 100° (212° F.) rapidly and with effervescence. The dilute substance, however, is comparatively stable, and may be boiled and even distilled without suffering decomposition. Yet it is liable to

explosive decomposition when exposed to summer temperature in closed vessels.

Hydrogen peroxid acts both as a reducing and an oxidizing agent. Arsenic, sulfids, and sulfur dioxid are oxidized by it at the expense of half its oxygen. When it is brought in contact with silver oxid both substances are violently decomposed, water and elementary silver remaining. By certain substances, such as gold, platinum, and charcoal in a state of fine division, fibrin, or manganese dioxid, it is decomposed with evolution of oxygen; the decomposing agent remaining unchanged.

The pure substance, when decomposed, yields 475 times its volume of oxygen; the dilute 15 to 20 volumes.

In dilute solution it is used as a bleaching agent and in the renovation of old oil-paintings. It is an energetic disinfectant and antiseptic, and is extensively used in surgery. "Ozonic ether" is a mixture of ethylic ether and dilute hydrogen peroxid.

**Analytical Characters.**—1. To a solution of starch a few drops of cadmium iodid solution are added, then a small quantity of the fluid to be tested, and, finally, a drop of a solution of ferrous sulfate. A blue color is produced in the presence of hydrogen peroxid, even if the solution contain only 0.05 milligram per litre.

2. Add freshly-prepared tincture of guaiacum and a few drops of a cold infusion of malt. A blue color—1 in 2,000,000.

3. Add to the liquid a few drops of potassium dichromate and a little dilute sulfuric acid, and agitate with ether. The ether assumes a brilliant blue-violet color.

4. Add to 6 cc. of the liquid sulfuric acid, iodid of zinc, starch-paste, two drops of a 2 per cent. solution of cupric sulfate, and a little one-half per cent. solution of ferrous sulfate, in the order named. A blue color.

5. Add a trace of acetic acid, some α naphthylamin and solid sodium chlorid. After a short time a blue or blue-violet color, and after some hours a flocculent ppt. of the same color.

**Atmospheric Hydrogen Dioxid.**—It has been claimed that atmospheric air, rain-water, snow, and hoar-frost constantly contain small quantities of hydrogen peroxid; the amount in rain-water varying from 0.0008 to 0.05 part in 100,000. The most recent experiments bearing upon the supposed presence of ozone and hydrogen peroxid in atmospheric air seem, however, to justify the belief that those substances, if present in air at all, are not met with in the amounts and with the constancy that have been claimed. According to this latter view the appearances from which the presence of ozone and hydrogen peroxid has been inferred are not caused by those substances, but by nitrous acid and the oxids of nitrogen.

## CLASS II—ACIDULOUS ELEMENTS.

**Elements all of whose Hydrates are Acids, and which do not form Salts with the Oxacids.**

# I. CHLORIN GROUP.

FLUORIN. CHLORIN. BROMIN. IODIN.

The elements of this group are univalent. With hydrogen they form acid compounds, composed of one volume of the element in the gaseous state with one volume of hydrogen. Mineral acids in which they occur are monobasic. The first two are gases, the third liquid, the fourth solid at ordinary temperatures. They are known as the **halogens.** The relations of their compounds to each other are shown in the following table:

| | | | | | | |
|---|---|---|---|---|---|---|
| HF | ——— | ——— | ——— | ——— | ——— | ——— |
| HCl | $Cl_2O$ | $Cl_2O_4$ | HClO | $HClO_2$ | $HClO_3$ | $HClO_4$ |
| HBr | ——— | ——— | HBrO | ——— | $HBrO_3$ | $HBrO_4$ |
| HI | ——— | $I_2O_4$ | HIO | $HIO_2$ | $HIO_3$ | $HIO_4$ |
| Hydro-ic acid. | Monoxid. | Tetroxid. | Hypo-ous acid | -ous acid. | -ic acid | Per-ic acid. |

## FLUORIN.

*Symbol*=F—*Atomic weight*=19 (O=16: 19; H=1: 18.85)—*Sp. gr.* 1.265 A (*calculated*=1.316)—*Discovered by Sir H. Davy in* 1812.

Fluorin has been isolated by the electrolysis of pure, dry HF at—23° (—9.4° F.). It exists in nature chiefly in *Fluor Spar*, $CaF_2$, and in *cryolite*, $Al_2F_6(NaF)_6$.

It is a gas, colorless in thin layers, greenish yellow in layers 50 cent. thick.

It decomposes $H_2O$, with formation of HF and ozone. In it Si, B, As, Sb, S, and I fire spontaneously. With H it detonates violently, even in the dark. It attacks organic substances violently. The apparatus in which it is liberated must be made of platinum or fluor-spar. It forms compounds with all other elements except oxygen.

**Hydrogen Fluorid.**—*Hydrofluoric acid*=HF—*Molecular weight* =20. Hydrofluoric acid is obtained by the action of an excess of sulfuric acid upon fluor-spar or upon barium fluorid, with the aid of gentle heat: $CaF_2+H_2SO_4=CaSO_4+2HF$. If a solution be desired, the operation is conducted in a platinum or lead retort, whose beak is connected with a U-shaped receiver of the same metal, which is cooled and contains a small quantity of water.

The pure acid is a colorless liquid, which boils at 19° (67°F.) and solidifies at—1° (30.2° F.). Sp. gr. 0.985 at 12° (53.6° F.). The aqueous acid is a colorless liquid, highly acid and corrosive, and having a penetrating odor. Great care must be exercised that neither the solution nor the gas come in contact with the skin, as they produce painful ulcers which heal with difficulty, and also constitutional symptoms which may last for days. The inhalation of air containing very small quantities of HF has caused permanent loss of voice, and in two cases, death. When the acid has accidentally come in contact with the skin the part should be washed with dilute solution of potash, and the vesicle which forms should be opened.

Both the gaseous acid and its solution remove the silica from glass, a property utilized in etching upon that substance, the parts upon which no action is desired being protected by a coating of wax.

The presence of fluorin in a compound is detected by reducing the substance to powder, moistening it with sulfuric acid in a platinum crucible, over which is placed a slip of glass prepared as above. At the end of half an hour the wax is removed from the glass, which will be found to be etched if the substance examined contained a fluorid.

## CHLORIN.

*Symbol*=Cl—*Atomic weight*=35.5 (O=16:35.45; H = 1:35.17)—*Molecular weight*=71 *Sp. gr.*=2.4502 *A—One litre weighs 3.17 grams —100 cubic inches weigh* 76.3 *grains—Name derived from* χλωρός= *yellowish green—Discovered by Scheele in* 1774.

**Occurrence.**—Only in combination, most abundantly in sodium chlorid.

**Preparation.**—(1) By heating together manganese dioxid and hydrochloric acid (Scheele): $MnO_2+4HCl=MnCl_2+2H_2O+Cl_2$.

This and similar operations are usually conducted in an apparatus such as that shown in Fig. 22. The earthenware vessel A (which on a small scale may be replaced by a glass flask) is two-thirds filled with lumps of manganese dioxid of the size of hazelnuts and adjusted in the water bath; hydrochloric acid is poured in through the safety-tube and the bath heated. The disengaged gas is caused to bubble through the small quantity of water in B, is then dried by passage over the fragments of calcium chlorid in C, and is finally collected by displacement of air in the vessel D.

When the vessel A has become half filled with liquid it is best to decant the solution of manganous chlorid, wash the remaining oxid with water and begin anew. A kilo of oxid yields 257.5 litres of Cl.

In a modification of this process, which permits of the more easy recovery of the manganese dioxid, nitric acid is used along with

hydrochloric. The reaction is: $2HCl+2HNO_3+MnO_2=Mn(NO_3)_2+2H_2O+Cl_2$. The $MnO_2$ and $HNO_3$ are recovered by heating the manganese nitrate to 190° (374° F.) and treating the vapor with air and steam. The reactions are: $Mn(NO_3)_2=MnO_2+N_2O_4$ and $N_2O_4+H_2O+O=2HNO_3$.

(2) By the action of manganese dioxid upon hydrochloric acid in the presence of sulfuric acid, manganous sulfate being also formed: $MnO_2+2HCl+H_2SO_4=MnSO_4+2H_2O+Cl_2$. The same quantity of chlorin is obtained as in (1), with the use of half the amount of hydrochloric acid.

(3) By heating a mixture of one part each of manganese dioxid and sodium chlorid, with three parts of sulfuric acid. Hydrochloric

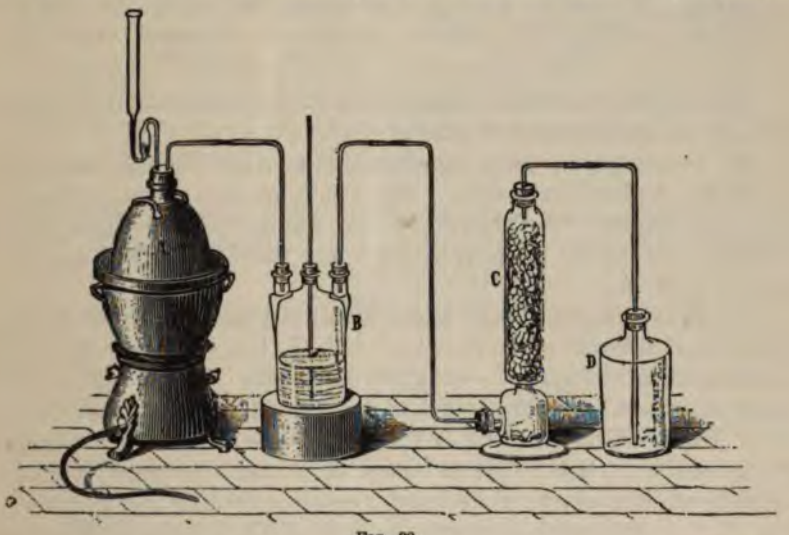



FIG. 22.

acid and sodium sulfate are first formed: $H_2SO_4+2NaCl=Na_2SO_4+2HCl$; and the acid is immediately decomposed by either of the reactions indicated in (1) and (2), according as sulfuric acid is or is not present in excess.

(4) By the action of potassium dichromate upon hydrochloric acid; potassium and chromic chlorids being also formed: $K_2Cr_2O_7+14HCl=2KCl+Cr_2Cl_6+7H_2O+3Cl_2$. Two parts of powdered dichromate are heated with 17 parts of acid of sp. gr. 1.16; 100 grams of the salt yielding 22.5 litres of Cl.

(5) A convenient method of obtaining chlorin on a laboratory scale is by the use of "chlorin cubes." These are made by pressing together 1 part of plaster of Paris and 4 parts of chlorid of lime (q. v.), cutting into small cubes and drying. The cubes are used in

one of the forms of constant apparatus (Figs. 18, 19, 20), with dilute hydrochloric acid, Cl being evolved at the ordinary temperature.

When a slow evolution of Cl, extending over a considerable period of time, is desired, as for ordinary disinfection, moistened chlorid of lime is exposed to the air, the calcium hypochlorite being decomposed by the atmospheric carbon dioxid. If a more rapid evolution of gas be desired, the chlorid of lime is moistened with dilute hydrochloric acid in place of with water.

(6) By the action of potassium chlorate upon hydrochloric acid Cl is liberated, slowly at the ordinary temperature, more rapidly at the temperature of the water-bath:

| $2KClO_3$ | + | $4HCl$ | = | $Cl_2$ | + | $Cl_2O_4$ | + | $2KCl$ | + | $2H_2O$. |
|---|---|---|---|---|---|---|---|---|---|---|
| Potassium chlorate. | | Hydrochloric acid. | | Chlorin. | | Chlorin tetroxid. | | Potassium chlorid. | | Water. |

(7) Chlorin is obtained industrially in the manufacture of caustic soda by the electrolysis of NaCl.

(8) In Deacon's process cupric oxid is used as a "contact substance" to oxidize hydrochloric acid. The reactions are: $2CuCl_2=Cu_2Cl_2+Cl_2$, then, $Cu_2Cl_2+O_2=2CuO+Cl_2$, and, finally, $2CuO+4HCl=2CuCl_2+2H_2O$. As the O is derived from air the Cl obtained is largely diluted with N.

(9) In the Solvay, Weldon and Mond processes Cl is derived from magnesium chlorid by the reaction: $2MgCl_2+O_2=2MgO+2Cl_2$.

**Properties.**—*Physical.*—A greenish yellow gas, at the ordinary temperature and pressure; it has a penetrating odor, and is, even when highly diluted, very irritating to the respiratory passages. Being soluble in $H_2O$ to the extent of one volume to three volumes of the solvent, it must be collected by displacement of air, as shown in Fig. 22. A saturated aqueous solution of Cl is known to chemists as **chlorin water**, and in pharmacy as **aqua chlori** (U. S.), **Liquor chlori** (Br.). It should bleach, but not redden, litmus paper. Under a pressure of 6 atmospheres at 0° (32° F.), or 8½ atmospheres at 12° (53.6° F.), Cl becomes an oily, yellow liquid, of sp. gr. 1.33; and boiling at—33.6° (—28.5° F.). Liquid chlorin, transported in lead-lined steel cylinders, is now an article of commerce.

*Chemical.*—Chlorin exhibits a great tendency to combine with other elements, with all of which, except F, O, N, and C, it unites directly, frequently with evolution of light as well as heat, and sometimes with an explosion. With H it combines slowly, to form hydrochloric acid, under the influence of diffuse daylight, and violently in direct sunlight, or in highly actinic artificial lights. A candle burns in Cl with a faint flame and thick smoke, its H combining with the Cl, while carbon becomes free.

At a red heat Cl decomposes $H_2O$ rapidly, with formation of hydrochloric, chloric, and probably hypochlorous acids. The same change takes place slowly under the influence of sunlight, hence chlorin water should be kept in the dark or in bottles of yellow glass.

In the presence of $H_2O$, chlorin is an active bleaching and disinfecting agent. It acts as an indirect oxidant, decomposing $H_2O$, the nascent O from which then attacks the coloring or odorous principle.

Chlorin is readily fixed by many organic substances, either by addition or substitution. In the first instance, as when Cl and olefiant gas unite to form ethylene chlorid, the organic substance simply takes up one or more atoms of chlorin: $C_2H_4+Cl_2=C_2H_4Cl_2$. In the second instance, as when Cl acts upon marsh gas to produce methyl chlorid: $CH_4+Cl_2=CH_3Cl+HCl$, each substituted atom of Cl displaces an atom of H, which combines with another Cl atom to form hydrochloric acid.

**Hydrogen Chlorid — Hydrochloric Acid — Muriatic Acid — Acidum Hydrochloricum** (U. S.; Br.)—HCl—*Molecular weight*= 36.5—*Sp. gr.* 1.259 *A—A litre weighs* 1.6293 *gram.*

**Occurrence.**—In volcanic gases and in the gastric juice of the mammalia.

**Preparation.**—(1) By the direct union of its constituent elements.

(2) By the action of sulfuric acid upon a chlorid, a sulfate being at the same time formed: $H_2SO_4+2NaCl=Na_2SO_4+2HCl$.

This is the reaction by which the HCl used in the arts is produced.

(3) Hydrochloric acid is also formed in a great number of reactions, as when Cl is substituted in an organic compound.

**Properties.**—*Physical.*—A colorless gas, acid in reaction and taste, having a sharp, penetrating odor, and producing great irritation when inhaled. It becomes liquid under a pressure of 40 atmospheres at 4° (39.2° F.) Its critical temperature is 52° (125.6° F.) and its critical pressure 83 atmospheres. It is very soluble in $H_2O$, one volume of which dissolves 480 volumes of the gas at 0° (32° F.)

*Chemical.*—Hydrochloric acid is neither combustible nor a supporter of combustion, although certain elements, such as K and Na, burn in it. It forms white clouds on contact with moist air.

**Solution of Hydrochloric Acid.**—It is in the form of aqueous solution that this acid is usually employed in the arts and in pharmacy. It is, when pure, a colorless liquid (yellow when impure), acid in taste and reaction, whose sp. gr. and boiling-point vary with the degree of concentration. When heated, it evolves HCl, if it contain more than 20 per cent. of that gas, and $H_2O$ if it con-

tain less. A solution containing 20 per cent. boils at 111° (232° F.), is of sp. gr. 1.099, has the composition $HCl+8H_2O$, and distils unchanged.

*Commercial muriatic acid* is a yellow liquid; sp. gr. about 1.16; contains 32 per cent. HCl; and contains ferric chlorid, sodium chlorid; and arsenical compounds.

*Acidum hydrochloricum* is a colorless liquid, containing small quantities of impurities. It contains 31.9 per cent. HCl and its sp. gr. is 1.16 (U. S.; Br.) The dilute acid is the above diluted with water. Sp. gr. 1.049 = 10 per cent HCl (U. S.); sp. gr. 1.052 = 10.5 per cent. HCl (Br.)

*C. P. (chemically pure) acid* is usually the same as the strong pharmaceutical acid and far from pure (see below). The strongest solution has a sp. gr. of 1.20 and contains 40.8 per cent. HCl.

Hydrochloric acid is classed, along with nitric and sulfuric acids, as one of three **strong mineral acids.** It is decomposed by many elements, with formation of a chlorid and liberation of hydrogen: $2HCl+Zn=ZnCl_2+H_2$. With oxids and hydroxids of the metals it enters into double decomposition, forming $H_2O$ and a chlorid: $CaO+2HCl=CaCl_2+H_2O$ or $CaH_2O_2+2HCl=CaCl_2+2H_2O$.

Oxidizing agents decompose HCl with liberation of Cl. A mixture of hydrochloric and nitric acids in the proportion of three molecules of the former to one of the latter (18 cc. $HNO_3$: 82 cc. HCl soln.), is the **acidum nitrohydrochloricum** (U. S.; Br.), or **aqua regia.** The latter name alludes to its power of dissolving gold, by combination of the nascent Cl, which it liberates, with that metal. to form the soluble auric chlorid (p. 111).

**Impurities.**—A chemically pure solution of this acid is exceedingly rare. The impurities usually present are: *Sulfurous acid*—hydrogen sulfid is given off when the acid is poured upon zinc; *Sulfuric acid*—a white precipitate is formed with barium chlorid; *Chlorin* colors the acid yellow; *Lead* gives a black color when the acid is treated with hydrogen sulfid; *Iron*—the acid gives a red color with ammonium thiocyanate; *Arsenic*—the method of testing by hydrogen sulfid is not sufficient. If the acid is to be used for toxicological analysis, a litre, diluted with half as much $H_2O$, and to which a small quantity of potassium chlorate has been added, is evaporated over the water bath to 400 cc.; 25 cc. of sulfuric acid are then added, and the evaporation continued until the liquid measures about 100 cc. This is introduced into a Marsh apparatus and must produce *no* mirror during an hour.

**Chlorids.**—A few of the chlorids are liquid, $SnCl_4$, $SbCl_5$; the remainder are solid, crystalline and more or less volatile. The metallic chlorids are soluble in water, except AgCl and $Hg_2Cl_2$, which

are insoluble, and $PbCl_2$, and $Cu_2Cl_2$, which are sparingly soluble. The chlorids of the non-metals are decomposed by $H_2O$.

The chlorids are formed: (1) By the direct union of the elements: $P+Cl_5=PCl_5$; (2) By the action of chlorin upon a heated mixture of oxid and carbon: $Al_2O_3+3C+3Cl_2=Al_2Cl_6+3CO$; (3) By solution of the metal, oxid, hydroxid, or carbonate in HCl: $Zn+2HCl=ZnCl_2+H_2$; (4) By double decomposition between a solution of a chlorid and that of another salt whose metal forms an insoluble chlorid: $AgNO_3+NaCl=AgCl+NaNO_3$.

**Analytical Characters.** — (1) With $AgNO_3$ a white, flocculent ppt., insoluble in $HNO_3$, soluble in $NH_4HO$. (2) With $Hg_2(NO_3)_2$, a white ppt., which turns black with $NH_4HO$.

**Toxicology.—Poisons and corrosives.—A poison is any substance which, being in solution in the blood, may produce death or serious bodily harm.**

**A corrosive is a substance capable of producing death by its chemical action upon a tissue with which it comes in direct contact.**

The corrosives act much more energetically when concentrated than when dilute; and when the dilution is great they have no deleterious action. The degree of concentration in which the true poisons are taken is of little influence upon their action if the dose taken remain the same.

Under the above definitions the strong mineral acids act as corrosives rather than as poisons. They produce their injurious results by destroying the tissues with which they come in contact, and will cause death as surely by destroying a large surface of skin, as when they are taken into the stomach.

The symptoms of corrosion by the mineral acids begin immediately, during the act of swallowing. The chemical action of the acid upon every part with which it comes in contact causes acute burning pain, extending from the mouth to the stomach and intestine, referred chiefly to the epigastrium. Violent and distressing vomiting of dark, tarry, or "coffee-ground," highly acid material is a prominent symptom. Eschars, at first white or gray, later brown or black, are formed where the acid has come in contact with the skin or mucous membrane. Respiration is labored and painful, partly by pressure of the abdominal muscles, but also, in the case of hydrochloric acid, from entrance of the irritating, acid gas into the respiratory passages. Death may occur within twenty-four hours, from collapse; more suddenly from perforation of large blood-vessels, or from peritonitis; or after several weeks, secondarily, from starvation, due to closure of the pylorus by inflammatory thickening, and destruction of the gastric glands.

The object of the treatment in corrosion by the mineral acids is to neutralize the acid and convert it into a harmless salt. For this purpose the best agent is magnesia (magnesia usta), suspended in a small quantity of water, or if this be not at hand, a strong solution of soap. Chalk and the carbonates and bicarbonates of sodium and potassium should not be given, as they generate large volumes of gas. The scrapings of a plastered wall, or oil, are entirely useless. Any attempt at the introduction of a tube into the œsophagus is attended with danger of perforation, except in the earliest stages of the intoxication.

**Compounds of Chlorin and Oxygen.**—Two compounds of chlorin and oxygen are known. They are both very unstable, and prone to sudden and violent decomposition.

**Chlorin Monoxid.**—$Cl_2O$—87—*Hypochlorous anhydrid* or *oxid*, is formed by the action, below 20° (68° F.), of dry Cl upon precipitated mercuric oxid: $HgO+2Cl_2=HgCl_2+Cl_2O$.

On contact with $H_2O$ it forms **hypochlorous acid**, HClO, which owing to its instability, is not used industrially, although the hypochlorites of Ca, K, and Na are.

**Chlorin Tetroxid**—*Chlorin peroxid*, $Cl_2O_4$—135—is a violently explosive body, produced by the action of sulfuric acid upon potassium chlorate. Below —20° (—4° F.) it is an orange-colored liquid; above that temperature a yellow gas. It explodes violently when heated to a temperature below 100° (212° F.), There is no corresponding hydrate known, and if it be brought in contact with an alkaline hydroxid, a mixture of chlorate and chlorite is formed.

Besides the above, two oxacids of Cl are known, the anhydrids corresponding to which have not been isolated.

**Chloric Acid**—$HClO_3$—84.5—obtained, in aqueous solution, as a strongly acid, yellowish, syrupy liquid, by decomposing its barium salt by the proper quantitity of sulfuric acid.

**Perchloric Acid**—$HClO_4$—100.5—is the most stable of the series. It is obtained by boiling potassium chlorate with hydrofluosilicic acid, decanting the cold fluid, evaporating until white fumes appear, decanting from time to time, and finally distilling. It is a colorless, oily liquid; sp. gr. 1.782; which explodes on contact with organic substances or charcoal.

## BROMIN.

**Bromum**, U. S., Br.—*Symbol*=Br.—*Atomic weight*=80—(O=16: 79.06; H=1: 79.32)—*Molecular weight*=160—*Sp. gr. of liquid*= 3.1872 at 0°; *of vapor*=5.52 *A*—*Freezing point*= —24.5° (—12.1° *F.*)—*Boiling point*=63° (145.4° *F.*)—*Name derived from* βρῶμος=*a stench*—*Discovered by Balard in* 1826.

**Occurrence.**—Only in combination, most abundantly with Na and Mg in sea water and the waters of mineral springs.

**Preparation.**—It is obtained from the mother liquors, left by the evaporation of sea water, and of that of certain mineral springs, and from sea weed. These are mixed with sulfuric acid and manganese dioxid and heated, when the bromids are decomposed by the Cl produced, and Br distils.

**Properties.**—*Physical.*—A dark reddish-brown liquid, volatile at all temperatures above —24.5° (—12.1° F.); giving off brown-red vapors which produce great irritation when inhaled. Soluble in water to the extent of 3.2 parts per 100 at 15° (59° F.); more soluble in alcohol, carbon disulfid, chloroform, and ether.

*Chemical.*— The chemical characters of Br are similar to those of Cl, but less active.—With $H_2O$ it forms a crystalline hydrate at 0° (32° F): $Br\,5H_2O$. Its aqueous solution is decomposed by exposure to light, with formation of hydrobromic acid.

It is highly poisonous.

**Hydrogen Bromid—Hydrobromic acid—Acidum hydrobromicum dil.** (U. S.) = HBr—*Molecular weight* = 81—*Sp. gr.* = 2.71 *A—A litre weighs* 3.63 *grams—Liquefies at* —69° (—92°.2 *F.*)—*Solidifies at*—73° (—99.4° *F.*).

**Preparation.**—This substance cannot be obtained from a bromid as HCl is obtained from a chlorid. It is produced, along with phosphorous acid, by the action of $H_2O$ upon phosphorus tribromid: $PBr_3+3H_2O=H_3PO_3+3HBr$; or by the action of Br upon paraffin.

**Properties.**—A colorless gas; produces white fumes with moist air; acid in taste and reaction, and readily soluble in $H_2O$, with which it forms a hydrate, $HBr\,2H_2O$. Its chemical properties are similar to those of HCl.

**Bromids** closely resemble the chlorids and are formed under similar conditions. They are decomposed by chlorin, with formation of a chlorid and liberation of Br: $2KBr+Cl_2=2KCl+Br_2$. The metallic bromids are soluble in $H_2O$, except AgBr and $Hg_2Br_2$, which are insoluble, and $PbBr_2$, which is sparingly soluble. The bromids of Mg, Al, Ca are decomposed into oxid and HBr on evaporation of their aqueous solutions.

**Analytical Characters.**—(1) With $AgNO_3$, a yellowish white ppt., insoluble in $HNO_3$, sparingly soluble in $NH_4HO$. (2) With chlorin water a yellow solution which communicates the same color to chloroform and to starch-paste.

**Oxacids of Bromin.**—No oxids of bromin are known, although three oxacids exist, either in the free state or as salts:

**Hypobromous Acid**—$HBrO$—=97—is obtained, in aqueous solution, by the action of Br upon mercuric oxid, silver oxid, or silver nitrate. When Br is added to concentrated solution of potassium hydroxid no hypobromite is formed, but a mixture of bromate and bromid, having no decolorizing action. With sodium hydroxid, however, sodium hypobromite is formed in solution; and such a solution, freshly prepared, is used in Knop's process for determining urea (q. v.).

**Bromic Acid**—$HBrO_3$—129—has only been obtained in aqueous solution, or in combination. It is formed by decomposing barium bromate with an equivalent quantity of sulfuric acid: $Ba(BrO_3)_2 + H_2SO_4 = 2HBrO_3 + BaSO_4$. In combination it is produced, along with the bromid, by the action of Br on caustic potassa: $3Br_2 + 6KHO = KBrO_3 + 5KBr + 3H_2O$.

**Perbromic Acid**—$HBrO_4$—145—is obtained as a comparatively stable, oily liquid, by the decomposition of perchloric acid by Br, and concentrating over the water-bath.

It is noticeable in this connection that, while HCl and the chlorids are more stable than the corresponding Br compounds the oxygen compounds of Br are more permanent than those of Cl.

## IODIN.

**Iodum** (U. S.; Br.)—*Symbol* = I — *Atomic weight*=127 (O=16: 126.85; H=1:125.84)—*Molecular weight*=254—*Sp. gr. of solid*= 4.948; *of vapor*=8.716 *A*—*Fuses at* 113.6° (236.5° *F.*)—*Boils at* 175° (347° *F.*) — *Name derived from* ἰώδης = *violet* — *Discovered by Courtois in* 1811.

**Occurrence.**—In combination with Na, K, Ca, and Mg, in sea-water, the waters of mineral springs, marine plants and animals. Cod-liver oil contains about 37 parts in 100,000.

**Preparation.**—It is obtained from the ashes of sea-weed, called *kelp* or *varech*. These are extracted with $H_2O$, and the solution evaporated to small bulk. The mother liquor, when separated from the other salts which crystallize out, contains the iodids, which are decomposed by Cl, aided by heat, and the liberated iodin is condensed.

**Properties.**—*Physical.*—Blue-gray, crystalline scales, having a metallic luster. Volatile at all temperatures, the vapor having a violet color, and a peculiar odor. It is sparingly soluble in $H_2O$, which, however, dissolves larger quantities on standing over an excess of iodin, by reason of the formation of hydriodic acid. The presence of certain salts, notably potassium iodid, increases the

solvent power of $H_2O$ for iodin. The **Liq. Iodi Comp.** (*U. S.*), **Liq. Iodi**, *Br.* is a solution of iodin in a solution of potassium iodid. Very soluble in alcohol; **Tinct. iodi** (*U. S.; Br.*), in ether, chloroform, benzene, and carbon disulfid. With the three last-named solvents it forms violet solutions, with the others brown solutions.

*Chemical.*—In its chemical characters I resembles Cl and Br, but is less active. It decomposes $H_2O$ slowly and is a weak bleaching and oxidizing agent. In presence of water, it decomposes hydrogen sulfid with formation of hydriodic acid, and liberation of sulfur. It does not combine directly with oxygen, but does with ozone. Potassium hydroxid solution dissolves it, with formation of potassium iodid, and some hypoiodite. Nitric acid oxidizes it to iodic acid. With ammonium hydroxid solution it forms the explosive nitrogen iodid.

**Impurities.**—*Non-volatile substances* remain when the I is heated. *Water* separates as a distinct layer when I is dissolved in carbon disulfid. *Cyanogen iodid* appears in white, acicular crystals among the crystals of sublimed I, when half an ounce of the substance is heated over the water-bath for twenty minutes, in a porcelain capsule, covered with a flat-bottomed flask filled with cold water. The last named is the most serious impurity, as it is actively poisonous.

**Toxicology.**—Taken internally, iodin acts both as a local irritant and as a true poison. It is discharged as an alkaline iodid by the urine and perspiration, and when taken in large quantity it appears in the fæces.

The poison should be removed as rapidly as possible by the use of the stomach pump and of emetics. Farinaceous substances may also be given.

**Hydrogen Iodid—Hydriodic acid**—HI—*Molecular weight*=127.85—*Sp. gr.* 4.443 A.

**Preparation.**—By the decomposition of phosphorus triiodid by water: $PI_3+3H_2O=H_3PO_3+3HI$. Or, in solution by passing hydrogen sulfid through water holding iodin in suspension: $H_2S+I_2=2HI+S$.

**Properties.**—A colorless gas, forming white fumes on contact with air, and of strongly acid reaction. Under the influence of cold and pressure it forms a yellow liquid, which solidifies at —55° (—67° F.). Water dissolves it to the extent of 425 volumes for each volume of the solvent at 10° (50° F.).

It is partly decomposed into its elements by heat. Mixed with O it is decomposed, even in the dark, with formation of $H_2O$ and liberation of I. Under the influence of sunlight the gas is slowly decomposed, although its solutions are not so affected, if they be free from

air. Chlorin and bromin decompose it, with liberation of iodin. With many metals it forms iodids. It yields up its H readily and is used in organic chemistry as a source of that element in the nascent state.

**Iodids** are formed under the same conditions as the chlorids and bromids, which they resemble in their properties. The metallic iodids are soluble in water—except AgI, $Hg_2I_2$, which are insoluble, and $PbI_2$, which is very slightly soluble. The iodids of the earth metals are decomposed into oxid and HI on evaporation of their aqueous solutions. Chlorin decomposes the iodids as it does the bromids.

**Analytical Characters.**—(1) With $AgNO_3$, a yellow ppt., insoluble in $HNO_3$, and in $NH_4HO$. (2) With fuming $HNO_3$ or with chlorin water, a yellow liquid, which colors starch-paste black or purple, and chloroform or carbon disulfid violet.

**Chlorids of Iodin.**—Chlorin and iodin combine with each other in two proportions: **Iodin monochlorid, or protochlorid**—ICl is a red-brown, oily, pungent liquid, formed by the action of dry Cl upon I, and distilling at 100° (212° F.). **Iodin trichlorid, or perchlorid**—$ICl_3$ is a yellow, crystalline solid, having an astringent, acid taste and a penetrating odor; very volatile; its vapor irritating; easily soluble in water. It is formed by saturating $H_2O$ holding I in suspension with Cl, and adding concentrated sulfuric acid. $ICl_3$ has been used as an antiseptic.

**Oxacids of Iodin.**—The best known of these are the highest two of the series—iodic and periodic acids.

**Iodic Acid**—$HIO_3$—176.85 is formed as an iodate, whenever I is dissolved in a solution of an alkaline hydroxid: $I_6+6KHO=KIO_3+5KI+3H_2O$. As the free acid, by the action of strong oxidizing agents, such as nitric acid, or chloric acid, upon I; or by passing Cl for some time through $H_2O$ holding I in suspension.

Iodic acid appears in white crystals, decomposable at 170° (338° F.), and quite soluble in $H_2O$, the solution having an acid reaction, and a bitter, astringent taste.

It is an energetic oxidizing agent, yielding up its O readily, with separation of elementary I or of HI. It is used as a test for the presence of morphin (*q. v.*).

**Periodic Acid**—$HIO_4$—191.85—is formed by the action of Cl upon an alkaline solution of sodium iodate. The sodium salt thus obtained is dissolved in nitric acid, treated with silver nitrate, and the resulting silver periodate is then decomposed with $H_2O$. From the solution the acid is obtained in colorless crystals, fusible at 130° (266° F.), very soluble in water, and readily decomposable by heat.

## II. SULFUR GROUP.

SULFUR. SELENIUM. TELLURIUM.

The elements of this group are bivalent in most of their compounds, in some they are quadrivalent or hexavalent. With hydrogen they form compounds composed of one volume of the element, in the form of vapor, with two volumes of hydrogen — the combination being attended with a condensation in volume of one-third. Mineral acids in which they occur are dibasic. They are all solids at ordinary temperatures. The relation of their compounds to each other is shown in the following table:

| | | | | | |
|---|---|---|---|---|---|
| $H_2S$ | $SO_2$ | $SO_3$ | $H_2SO_2$ | $H_2SO_3$ | $H_2SO_4$ |
| $H_2Se$ | $SeO_2$ | $SeO_3$ | —— | $H_2SeO_3$ | $H_2SeO_4$ |
| $H_2Te$ | $TeO_2$ | $TeO_3$ | —— | $H_2TeO_3$ | $H_2TeO_4$ |
| Hydro-ic acid. | Dioxid. | Trioxid. | Hypo-ous acid. | -ous acid. | -ic acid. |

### SULFUR.

*Symbol* = S — *Atomic weight* = 32 (O = 16 : 32.06; H = 1 : 31.8) — *Molecular weight* = 64 — *Sp. gr. of vapor* = 2.22 A — *Fuses at* 114° (237.2° F.) — *Boils at* 447.3° (837° F.).

**Occurrence.** — Free in crystalline powder, large crystals, or amorphous, in volcanic regions. In combination in sulfids and sulfates, and in protein substances.

**Preparation.** — By purification of the native sulfur or decomposition of *pyrites*, natural sulfids of iron.

*Crude sulfur* is the product of the first distillation. A second distillation, in more perfectly constructed apparatus, yields *refined sulfur*. During the first part of the distillation, while the air of the condensing chamber is still cool, the vapor of S is suddenly condensed into a fine, crystalline powder, which is **flowers of sulfur, sulfur sublimatum** (*U. S.*). Later, when the temperature of the condensing chamber is above 114°, the liquid S collects at the bottom, whence it is drawn off and cast into sticks of **roll sulfur.**

**Properties.**—*Physical.*—Sulfur is usually yellow in color. At low temperature, and in minute subdivision, as in the precipitated **milk of sulfur, sulfur præcipitatum** (*U. S.*), it is almost or quite colorless. Its taste and odor are faint but characteristic. At 114° (237.2° F) it fuses to a thin yellow liquid, which at 150°–160° (302°–320° F.) becomes thick and brown; at 330°–340° (626–642.2° F.) it again becomes thin and light in color; finally it boils, giving off brownish yellow vapor at a temperature variously stated

between 440° (824° F.) and 448° (838.4° F.). If heated to about 400° (752° F.) and suddenly cooled, it is converted into **plastic sulfur**, which may be moulded into any desired form. It is insoluble in water, sparingly soluble in anilin, phenol, benzene, petroleum ether, and chloroform; readily soluble in sulfur chlorid, $S_2Cl_2$, and carbon disulfid. It dissolves in hot alcohol, and crystallizes from the solution, on cooling, in white prismatic crystals. It is dimorphous. When fused sulfur crystallizes it does so in oblique rhombic prisms. Its solution in carbon disulfid deposits it on evaporation in rhombic octahedra. The prismatic variety is of sp. gr. 1.95 and fuses at 120° (248° F.); the sp. gr. of the octahedral is 2.05 and its fusing point 114.5° (238° F.). The prismatic crystals, by exposure to air, become opaque, by reason of a gradual conversion into octahedra.

*Chemical.*—Sulfur unites readily with other elements, especially at high temperatures. Heated in air or O, it burns with a blue flame to sulfur dioxid, $SO_2$. In H it burns with formation of hydrogen sulfid, $H_2S$. The compounds of S are similar in constitution, and to some extent in chemical properties, to those of O. In many organic substances S may replace O; as in thiocyanic acid, CNSH, corresponding to cyanic acid, CNOH. Such compounds are designated by the syllable *thio;* the syllable *sulfo*, in the name of a compound, indicates that it contains the bivalent group, $SO_2$.

Sulfur is used principally in the manufacture of gunpowder; also to some extent in making sulfuric acid, sulfur dioxid, and matches, and for the prevention of fungoid and parasitic growths

**Hydrogen Monosulfid—Sulfhydric acid—*Hydrosulfuric acid*—Sulfuretted hydrogen—$H_2S$—*Molecular weight*=34—*Sp. gr.*=1.19 A.**

**Occurrence.**—In volcanic gases; as a product of the decomposition of organic substances containing S; in solution, in the waters of some mineral springs; and, occasionally, in small quantity, in the gases of the intestine. It is produced from proteins and other organic substances containing S by microbic action (sulfhydric fermentation).

**Preparation.**—(1) By direct union of the elements; either by burning S in H, or by passing H through molten S.

(2) By the action of nascent H upon sulfuric acid, if the mixture become heated. (See Marsh test for arsenic.)

(3) By the action of HCl upon antimony trisulfid: $Sb_2S_3+6HCl=2SbCl_3+3H_2S$.

(4) By the action of dilute sulfuric acid upon ferrous sulfid: $FeS+H_2SO_4=FeSO_4+H_2S$. This is the method generally used. The gas should be purified by passage over dry calcium chlorid, then through a tube, 20 cent. long, loosely filled with solid iodin, and,

finally, through a solution of potassium sulfid. The purpose of the iodin is to arrest traces of hydrogen arsenid, which may be present.

(5) By the action of HCl upon calcium sulfid: $CaS+2HCl=CaCl_2+H_2S$.

**Properties.**—*Physical.*—A colorless gas having the odor of rotten eggs and a disgusting taste; soluble in $H_2O$ to the extent of 3.23 parts to 1 at 15° (59° F.); soluble in alcohol. Under 17 atmospheres pressure, or at —74° (—101.2° F.) at the ordinary pressure, it liquefies; at —85.5° (—122° F.) it forms white crystals.

*Chemical.*—Burns in air with formation of sulfur dioxid and water: $2H_2S+3O_2=2SO_2+2H_2O$. If the supply of oxygen be deficient, $H_2O$ is formed, and sulfur liberated: $2H_2S+O_2=2H_2S+S_2$. Mixtures of $H_2S$ and air or O explode on contact with flame. Solutions of the gas when exposed to air become oxidized with deposition of S. Such solutions should be made with boiled $H_2O$, and kept in bottles which are completely filled, and well corked. Oxidizing agents, Cl, Br, and I remove its H with deposition of S. Hydrogen sulfid and sulfur dioxid mutually decompose each other into water, pentathionic acid and sulfur: $4SO_2+3H_2S=2H_2O+H_2S_5O_6+S_2$.

When the gas is passed through a solution of an alkaline hydroxid its S displaces the O of the hydroxid to form a sulfhydrate: $H_2S+KHO=H_2O+KHS$. With solutions of metallic salts $H_2S$ usually relinquishes its S to the metal: $CuSO_4+H_2S=CuS+H_2SO_4$, a property which renders it of great value in analytical chemistry.

**Physiological.**—Hydrogen sulfid is produced in the intestine by the decomposition of protein substances or of taurochloric acid; it also occurs sometimes in abscesses, and in the urine in tuberculosis, variola, and cancer of the bladder. It may also reach the bladder by diffusion from the rectum.

**Toxicology.**—An animal dies almost immediately in an atmosphere of pure $H_2S$, and the diluted gas is still rapidly fatal. An atmosphere containing 1 per cent may be fatal to man, although individuals habituated to its presence can exist in an atmosphere containing 3 per cent. Even when highly diluted it produces a condition of low fever, and care is to be taken that the air of laboratories in which it is used shall not become contaminated with it. Its toxic powers are due primarily, if not entirely, to its power of reducing and combining with the blood-coloring matter.

The form in which hydrogen sulfid generally produces deleterious effects is as a constituent of the gases emanating from sewers, privies, burial vaults, etc. These give rise to either slow poisoning, as when sewer gases are admitted to sleeping and other apartments by defective plumbing. or to sudden poisoning, as when a person enters a vault or other locality containing the noxious atmosphere.

The treatment should consist in promoting the inhalation of pure air, artificial respiration, cold affusions, and the administration of stimulants.

After death the blood is found to be dark in color, and gives the spectrum shown in Fig. 23, due to sulfhæmoglobin.

**Sulfids and Hydrosulfids.**—These compounds bear the same relation to sulfur that the oxids and hydroxids do to oxygen. The two sulfids of arsenic, $As_2S_3$ and $As_2S_5$, correspond to the two oxids, $As_2O_3$ and $As_2O_5$, and the potassium hydrosulfid, KHS, corresponds to the hydroxid, KHO.

Many metallic sulfids occur in nature, and are important ores of the metals, as the sulfids of zinc, mercury, cobalt, nickel, and iron. They are formed artificially, either by direct union of the elements at elevated temperatures, as in the case of iron: $Fe+S=FeS$; or by reduction of the corresponding sulfate, as in the case of calcium: $CaSO_4+2C=CaS+2CO_2$.

The sulfids are insoluble in $H_2O$, except those of the alkali metals. Many of the sulfids are soluble in alkaline liquids, and behave as

FIG. 23.

**thio-anhydrids,** forming thio-salts, corresponding to the oxysalts. Thus potassium arsenate, $K_3AsO_4$, and thioarsenate, $K_3AsS_4$; antimonate, $K_3SbO_4$, and thioantimonate, $K_3SbS_4$.

The metallic sulfids are decomposed when heated in air, usually with the formation of sulfur dioxid and the metallic oxid; sometimes with the formation of the sulfate; and sometimes with the liberation of the metal, and the formation of sulfur dioxid. The strong mineral acids decompose the sulfids with formation of hydrogen monosulfid.

**Analytical Characters.**—*Hydrogen Sulfid.*—(1) Blackens paper moistened with lead acetate solution. (2) Has an odor of rotten eggs.

*Sulfids.*—(1) Heated in the oxidizing flame of the blowpipe, give a blue flame and odor of $SO_2$. (2) With a mineral acid give off $H_2S$ (except sulfids of Hg, Au, and Pt).

**Hydrogen Polysulfids.**—Several other compounds of S and H, corresponding to the polysulfids of K, Na, and Ca, are known. The most stable is **hydrogen pentasulfid,** $H_2S_5$, which can only exist in the absence of water and at low temperatures.

**Sulfur and the Halogens.**—But one compound of S and Cl exists: **Sulfurous chlorid,** $S_2Cl_2$, formed when S is distilled in an atmosphere of Cl. It is a yellow, fuming liquid, used as a solvent for S. Several oxychlorids are also known.

**Bromin** in contact with excess of S forms a red liquid which consists principally of $S_2Br_2$.

**The iodid,** $S_2I_2$, is obtained by heating together 32 parts S and 127 parts I. It is a steel-gray, crystalline substance, fusible at 60° (140° F.), insoluble in water; and has been used in medicine.

**Sulfur Dioxid.**—*Sulfurous oxid*, or *anhydrid*—**Acidum sulfurosum** (U. S.; Br.)—$SO_2$—*Molecular weight*=64—*Sp. gr. of gas*=2.213; *of liquid*=1.45—*Boils at* —10° (14° *F.*); *solidifies at* —75° (—103° *F.*).

**Occurrence.**—In volcanic gases and in solution in some mineral waters.

**Preparation.**—(1) By burning S in air or O.

(2) By roasting iron pyrites in a current of air.

(3) During the combustion of coal or coal-gas containing S or its compounds.

(4) By heating sulfuric acid with copper: $2H_2SO_4+Cu=CuSO_4+2H_2O+SO_2$.

(5) By heating sulfuric acid with charcoal: $2H_2SO_4+C=2SO_2+CO_2+2H_2O$.

(6) By decomposing calcium sulfite, made into cubes with plaster of Paris, by HCl, at the ordinary temperature.

When the gas is to be used as a disinfectant it is usually obtained by reaction (1); in sulfuric acid factories (2) is used; (3) indicates the method in which atmospheric $SO_2$ is chiefly produced; in the laboratory (4) and (6) are used; (5) is the process directed by the U. S. and Br. Pharmacopœias.

**Properties.**—*Physical.*—A colorless, suffocating gas, having a disagreeable and persistent taste. Very soluble in $H_2O$, which at 15° (59° F.) dissolves about 40 times its volume (see below); also soluble in alcohol. At —10° (14° F.) it forms a colorless, mobile, transparent liquid, by whose rapid evaporation a cold of —65° (—85° F.) is obtained. Liquid $SO_2$ packed in sealed tins or in syphons, is now a commercial article.

*Chemical.* Sulfur dioxid is neither combustible nor a supporter of combustion. Heated with H it is decomposed: $SO_2+2H_2=S+2H_2O$. With nascent hydrogen, $H_2S$ is formed: $SO_2+3H_2=H_2S+2H_2O$.

Water not only dissolves the gas, but combines with it to form the true sulfurous acid, $H_2SO_3$. With solutions of metallic hydroxids it forms metallic sulfites: $SO_2+KHO=KHSO_3$; or $SO_2+2KHO=$

$K_2SO_3+H_2O$. A hydrate having the composition $H_2SO_3$, $8H_2O$ has been obtained as a crystalline solid, fusible at +4° (39.2° F.).

Sulfur dioxid and sulfurous acid solution are powerful reducing agents, being themselves oxidized to sulfuric acid: $SO_2+H_2O+O=H_2SO_4$; or $H_2SO_3+O=H_2SO_4$. It reduces nitric acid with formation of sulfuric acid and nitrogen tetroxid: $SO_2+2HNO_3=H_2SO_4+N_2O_4$. It decolorizes organic pigments, without, however, destroying the pigment, whose color may be restored by an alkali or a stronger acid. It destroys $H_2S$, acting, in this instance, not as a reducing but as an oxidizing agent: $4SO_2+3H_2S=2H_2O+H_2S_5O_6+S_2$. With Cl it combines directly under the influence of sunlight to form **sulfuryl chlorid** $(SO_2)''Cl_2$.

**Analytical Characters.**—(1) Odor of burning sulfur.

(2) Paper moistened with starch paste and iodic acid solution turns blue in air containing 1 in 3,000 of $SO_2$.

**Sulfur Trioxid**—*Sulfuric oxid or anhydrid*—$SO_3$—*Molecular weight* =80—*Sp. gr.* 1.95.

**Preparation.**—(1) By union of $SO_2$ and O at 250°-300° (482°-572° F.) or in presence of spongy platinum.

(2) By heating sulfuric acid in presence of phosphoric anhydrid: $H_2SO_4+P_2O_5=SO_3+2HPO_3$.

(3) By heating dry sodium pyrosulfate: $Na_2S_2O_7=Na_2SO_4+SO_3$.

(4) By heating pyrosulfuric acid below 100° (212°F.), in a retort fitted with a receiver, cooled by ice and salt: $H_2S_2O_7=H_2SO_4+SO_3$.

**Properties.**—White, silky, odorless crystals which give off white fumes in damp air. It unites with $H_2O$ with a hissing sound, and elevation of temperature, to form sulfuric acid. When dry it does not redden litmus.

Sulfur trioxid exists in two isomeric (see isomerism) modifications, being one of the few instances of isomerism among mineral substances. The $\alpha$ modification, liquid at summer temperature, solidifies in colorless prisms at 16° (60.8° F.) and boils at 46° (114.8° F.). The $\beta$ isomere is a white, crystalline solid which gradually fuses and passes into the $\alpha$ form at about 50° (122° F.)

## Oxacids of Sulfur.

| | |
|---|---|
| $H_2SO_2$ Hyposulfurous acid. | $H_2S_2O_7$ Pyrosulfuric acid. |
| $H_2SO_3$ Sulfurous acid. | $H_2S_2O_6$ Dithionic acid. |
| $H_2SO_4$ Sulfuric acid. | $H_2S_3O_6$ Trithionic acid. |
| $H_2S_2O_8$ Persulfuric acid. | $H_2S_4O_6$ Tetrathionic acid. |
| $H_2S_2O_3$ Thiosulfuric acid. | $H_2S_5O_6$ Pentathionic acid. |

**Hyposulfurous Acid**—$H_2SO_2$—66.—*Hydrosulfurous acid*—Is an unstable body known only in solution, obtained by the action of zinc upon solution of sulfurous acid. It is a powerful bleaching and deoxidizing agent.

**Sulfurous Acid**—$H_2SO_3$—82.—Although sulfurous acid has not been isolated, it, in all probability, exists in the acid solution, formed when sulfur dioxid is dissolved in water: $SO_2+H_2O=SO_3H_2$. Its salts, the sulfites, are well defined. From the existence of certain organic derivatives (see sulfonic acids) it would seem that two isomeric modifications of the acid may exist. They are distinguished as the *symmetrical*, in which the S atom is quadrivalent.

$$O=S\begin{matrix}OH\\OH\end{matrix},$$

and the *unsymmetrical*, in which the S atom is hexavalent.

$$\begin{matrix}O\\O\end{matrix}\!\!>\!S\begin{matrix}H\\OH\end{matrix}.$$

**Sulfites.**—The sulfites are decomposed by the stronger acids, with evolution of sulfur dioxid. Nitric acid oxidizes them to sulfates. The sulfites of the alkali metals are soluble, and are active reducing agents.

**The analytical characters** of the sulfites are: (1) With HCl they give off $SO_2$. (2) With zinc and HCl they give off $H_2S$. (3) With $AgNO_3$ they form a white ppt., soluble in excess of sulfite, and depositing metallic Ag when the mixture is boiled. (4) With $Ba(NO_3)_2$ they form a white ppt., soluble in HCl. If chlorin water be added to the solution so formed a white ppt., insoluble in acids, is produced.

**Sulfuric Acid—Oil of Vitriol—Acidum sulfuricum** (U. S.; Br.)—$H_2SO_4$—98.

**Preparation.**—(1) By the union of sulfur trioxid and water: $SO_3+H_2O=H_2SO_4$.

(2) By the oxidation of $SO_2$ or of S in the presence of water: $2SO_2+2H_2O+O_2=2H_2SO_4$; or $S_2+2H_2O+3O_2=2H_2SO_4$.

The manufacture of $H_2SO_4$ may be said to be the basis of all chemical industry, as there are but few processes in chemical technology into some part of which it does not enter. The method followed at present, the result of gradual improvement, may be divided into two stages: (1) the formation of a dilute acid; (2) the concentration of this product.

The first part is carried on in immense chambers of timber, lined with lead, and furnishes an acid having a sp. gr. of 1.55, and containing 65 per cent of true sulfuric acid, $H_2SO_4$. Into these chambers $SO_2$, obtained by burning sulfur, or by roasting pyrites, is

driven, along with a large excess of air. In the chambers it comes in contact with nitric acid, at the expense of which it is oxidized to $H_2SO_4$, while nitrogen tetroxid (red fumes) is formed: $SO_2+2HNO_3=H_2SO_4+N_2O_4$. Were this the only reaction, the disposal of the red fumes would present a serious difficulty and the amount of nitric acid consumed would be very great. A second reaction occurs between the red fumes and $H_2O$, which is injected in the form of steam, by which nitric acid and nitrogen dioxid are produced: $3N_2O_4+2H_2O=4HNO_3+2NO$. The nitrogen dioxid in turn combines with O to produce the tetroxid, which then regenerates a further quantity of nitric acid, and so on. This series of reactions is made to go on continuously, the nitric acid being constantly regenerated, and acting merely as a carrier of O from the air to the $SO_2$, in such manner that the sum of the reactions may be represented by the following equation: $2SO_2+2H_2O+O_2=2H_2SO_4$.

The acid is allowed to collect in the chambers until it has the sp. gr. 1.55, when it is drawn off. This *chamber acid*, although used in a few industrial processes, is not yet strong enough for most purposes. It is concentrated, first, by evaporation in shallow leaden pans, until its sp. gr. reaches 1.746. At this point it begins to act upon the lead, and is transferred to platinum stills, where the concentration is completed.

**Varieties.**—Sulfuric acid is met with in several conditions of concentration and purity:

(1) The *commercial oil of vitriol*, largely used in manufacturing processes, is a more or less deeply colored, oily liquid, varying in sp. gr. from 1.833 to 1.842, and in concentration from 93 per cent to 99½ per cent of true $H_2SO_4$.

(2) *C. P. acid*=**Acidum sulfuricum** (U. S.; Br.), of sp. gr. 1.84, colorless and comparatively pure (see below).

(3) *Glacial sulfuric acid* is a hydrate of the composition $H_2SO_4$, $H_2O$, sometimes called *bihydrated sulfuric acid*, which crystallizes in rhombic prisms, fusible at +8.5° (47.3° F.) when an acid of sp. gr. 1.788 is cooled to that temperature.

(4) *Ac. sulf. dil.* (U. S.; Br.) is a dilute acid of sp. gr. 1.069 and containing between 9 and 10 per cent. $H_2SO_4$ (U. S.), or of sp. gr. 1,094, containing between 12 and 13 per cent. $H_2SO_4$ (Br.).

**Properties.**—*Physical.*—A colorless, heavy, oily liquid; sp. gr. 1.842 at 12° (53.7° F.); crystallizes at 10.5° (50.9° F.); boils at 338° (640.4° F.). It is odorless, intensely acid in taste and reaction, and highly corrosive. It is non-volatile at ordinary temperatures. Mix-

tures of the acid with $H_2O$ have a lower boiling point, and lower sp. gr. as the proportion of $H_2O$ increases.

*Chemical.*—At a red heat vapor of $H_2SO_4$ is partly dissociated into $SO_3$ and $H_2O$; or, in the presence of platinum, into $SO_2$, $H_2O$ and O. When heated with S, C, P, Hg, Cu, or Ag, it is reduced with formation of $SO_2$.

Sulfuric acid has a great tendency to absorb $H_2O$, the union being attended with elevation of temperature, increase of bulk, and diminution of sp. gr. of the acid, and contraction of volume of the mixture. Three parts, by weight, of acid of sp. gr. 1.842, when mixed with one part of $H_2O$ produce an elevation of temperature to 130° (266° F.), and the resulting mixture occupies a volume 1-6 less than the sum of the volumes of the constituents. Strong $H_2SO_4$ is a good desiccator of air or gases. It should not be left exposed in uncovered vessels, lest by increase of volume it overflow. When it is to be diluted with $H_2O$, the acid should be added to the $H_2O$ in a vessel of thin glass, to avoid the projection of particles, or the rupture of the vessel. It is by virtue of its affinity for $H_2O$ that $H_2SO_4$ chars or dehydrates organic substances. Sulfuric acid is a powerful dibasic acid.

**Impurities.**—The commercial acid is so impure that it is only fit for manufacturing and the coarsest chemical uses. The so-called C. P. acid may further contain: *Lead;* becomes cloudy when mixed with ten times its volume of $H_2O$, if the quantity of Pb be sufficient. The dilute acid gives a black color with $H_2S$. *Salts ;* leave a fixed residue when the acid is evaporated. *Sulfur dioxid;* gives off $H_2S$ when the acid, diluted with an equal volume of $H_2O$, comes in contact with Zn. *Carbon ;* communicates a brown color to the acid. *Arsenic;* is very frequently present. When the acid is to be used for toxicological analysis, the test by $H_2S$ is not sufficient. The acid, diluted with an equal volume of $H_2O$, is to be introduced into a Marsh apparatus, in which no visible stain should be produced during an hour. *Oxids of nitrogen* are almost invariably present; they communicate a pink or red color to pure brucin.

**Sulfates.**—Sulfuric acid being dibasic, there exist two sulfates of the univalent metals: $HKSO_4$ and $K_2SO_4$, and but one sulfate of each bivalent metal: $CaSO_4$. The sulfates of Ba, Ca, Sr, and Pb are insoluble, or very sparingly soluble, in $H_2O$. Other sulfates are soluble in $H_2O$, but all are insoluble in alcohol.

**Analytical Characters.**—(1) Barium chlorid (or nitrate); a white ppt., insoluble in acids. The ppt., dried and heated with charcoal, forms BaS, which, with HCl, gives off $H_2S$. (2) Plumbic acetate forms a white ppt., insoluble in dilute acids. (3) Cal-

cium chlorid forms a white ppt., either immediately, or upon dilution with two volumes of alcohol; insoluble in dilute HCl or $HNO_3$.

**Toxicology.**—Sulfuric acid is an active corrosive, and may be, if taken in sufficient quantity in a highly diluted state, a true poison. The concentrated acid causes death, either within a few hours, by corrosion and perforation of the walls of the stomach and œsophagus, or, after many weeks, by starvation, due to destruction of the gastric mucous membrane and closure of the pyloric orifice of the stomach.

The treatment is the same as that for corrosion by HCl (see page 86).

**Persulfuric Acid.**—$H_2S_2O_8$—194—is formed by the electrolysis of concentrated sulfuric acid: $2H_2SO_4=H_2S_2O_8+H_2$; or by the action of hydrogen peroxid on sulfuric acid: $2H_2SO_4+H_2O_2=H_2S_2O_8+2H_2O$. It crystallizes at 0° in long, transparent needles. The corresponding anhydrid, $S_2O_7$, is formed by the action of high tension electric currents in a mixture of dry $SO_2$ and O.

**Thiosulfuric Acid.**—*Hyposulfurous acid*—$H_2S_2O_3$—114—may be considered as sulfuric acid, $H_2SO_4$, in which one atom of oxygen has been replaced by one of sulfur. The acid itself has not been isolated, being decomposed, on liberation from the thiosulfates, into sulfur, water, and sulfur dioxid: $H_2S_2O_3=S+SO_2+H_2O$.

**Pyrosulfuric Acid.**—*Fuming sulfuric acid—Nordhausen oil of vitriol—Disulfuric hydrate*—$H_2S_2O_7$—*Molecular weight*=178—*Sp. gr.* =1.9—*Boils at* 52.2° (126° *F*).

**Preparation.**—By distilling ferrous sulfate; and purification of the product by repeated crystallizations and fusions, until a substance fusing at 35° (95° F.) is obtained.

**Properties.**—The commercial Nordhausen acid, which is a mixture of $H_2S_2O_7$ with excess of $SO_3$, or of $H_2SO_4$, is a brown, oily liquid, which boils below 100° (212° F-) giving off $SO_3$; and is solid or liquid according to the temperature. It is used chiefly as a solvent for indigo, and in the anilin industry.

## SELENIUM AND TELLURIUM.

Se—78.5 Te—126.

These are rare elements which form compounds similar to those of sulfur. Elementary selenium is used in some forms of electrical apparatus.

# III. NITROGEN GROUP.

NITROGEN—PHOSPHORUS—ARSENIC—ANTIMONY.

The elements of this group are trivalent or quinquivalent, occasionally univalent. With hydrogen they form non-acid compounds, composed of one volume of the element in the gaseous state with three volumes of hydrogen, the union being attended with a condensation of volume of one-half.

Bismuth, frequently classed in this group, is excluded, owing to the existence of the nitrate $Bi(NO_3)_3$. The relations existing between the compounds of the elements of this group are shown in the following table:

| | | | | | | |
|---|---|---|---|---|---|---|
| $NH_3$, | $N_2O$, | NO, | $N_2O_3$, | $NO_2$, | $N_2O_5$, | — |
| $PH_3$, | — | — | $P_2O_3$, | — | $P_2O_5$, | $H_3PO_2$, |
| $AsH_3$, | — | — | $As_2O_3$, | — | $As_2O_5$, | — |
| $SbH_3$, | — | — | $Sb_2O_3$, | $Sb_2O_4$ | $Sb_2O_5$, | — |
| Hyd-rid. | Mon-oxid. | Di-oxid. | Tri-oxid. | Tetr-oxid. | Pent-oxid. | Hypo-ous acid. |
| — | — | $HNO_2$, | — | — | $HNO_3$, | |
| $H_3PO_3$, | $H_4P_2O_5$, | — | $H_3PO_4$, | $H_4P_2O_7$, | $HPO_3$, | |
| $H_3AsO_3$, | $H_4As_2O_5$, | $HAsO_2$, | $H_3AsO_4$, | $H_4As_2O_7$, | $HAsO_3$, | |
| — | — | $HSbO_2$, | $H_3SbO_4$, | $H_4Sb_2O_7$, | $HSbO_3$, | |
| -ous acid. | Pyro-ous acid. | Meta-ous acid. | -ic acid. | Pyro-ic acid. | Meta-ic acid. | |

## NITROGEN.

*Azote—Symbol*=N—*Atomic weight*=14 (O=16:14.04; H=1:13.93)—*Molecular weight*=28—*Sp. gr.*=0.9701—*One litre weighs* 1.254 *grams—Name from* νίτρον=nitre, γένεσις=*source; or from* ἀ, *privative* ζωή=*life—Discovered by Mayow in* 1669.

**Occurrence.**—Free in atmospheric air and in volcanic gases. In combination in the nitrates, in ammoniacal compounds and in a great number of animal and vegetable substances.

**Preparation.**—(1) By removal of O from atmospheric air; by burning P in air, or by passing air slowly over red-hot copper. It is contaminated with $CO_2$, $H_2O$, etc.

(2) By passing Cl through excess of ammonium hydroxid solution. If ammonia be not maintained in excess, the Cl reacts with the ammonium chlorid formed, to produce the explosive nitrogen chlorid.

(3) By heating ammonium nitrite $(NH_4)NO_2$: or a mixture of ammonium chlorid and potassium nitrite.

**Properties.**—A colorless, odorless, tasteless, non-combustible

gas; not a supporter of combustion; very sparingly soluble in water.

It is very slow to enter into combination, and most of its compounds are very prone to decomposition, which may occur explosively or slowly. Nitrogen combines directly with O under the influence of electric discharges; and with H under like conditions, and, directly, during the decomposition of nitrogenized organic substances. It combines directly with magnesium, boron, vanadium, and titanium

Nitrogen is not poisonous, but is incapable of supporting respiration.

**Argon.**—A substance discovered by Rayleigh and Ramsay in 1894 in the atmosphere. It is probably an element, although it may be an allotropic modification of nitrogen. It is a transparent, odorless, tasteless gas, sp. gr.=19.941. At the ordinary pressure it liquefies at—186.9° (—304.5° F.), forming a colorless liquid of sp. gr. 1.5. It solidifies at —190° (—311.3° F.). It is sparingly soluble in water: 4.05 in 100. No compounds of argon are known.

**Atmospheric Air.**—The alchemists considered air as an element, until Mayow, in 1669, demonstrated its complex nature. It was not, however, until 1770 that Priestley repeated the work of Mayow; and that the compound nature of air, and the characters of its constituents were made generally known by the labors (1770–1781) of Priestley, Rutherford, Lavoisier, and Cavendish. The older chemists used the terms *gas* and *air* as synonymous.

**Composition.**—Air is not a chemical compound, but a mechanical mixture of O and N, with smaller quantities of other gases. Leaving out of consideration vapor of water and small quantities of other gases, except 0.03 of carbon dioxid, air consists of 20.95 O and 79.02 N (including argon), by volume; or about 23 O and 77 N, by weight; proportions which vary but very slightly at different times and places; the extremes of the proportion of O found having been 20.908 and 20.999.

That air is not a compound is shown by the fact that the proportion of its constituents does not represent a relation between their atomic weights, or between any multiples thereof; as well as by the solubility of air in water. Were it a compound it would have a definite degree of solubility of its own, and the dissolved gas would have the same composition as when free. But each of its constituents dissolves in $H_2O$ according to its own solubility, and air dissolved in $H_2O$ at 14.1° (57.4° F.) consists of N and O, not in the proportion given above, but in the proportion of 66.76 to 33.24.

Besides these two main constituents, air contains about 4–5 thousandths of its bulk of other substances; vapor of water, carbon dioxid, ammoniacal compounds, hydrocarbons, ozone, oxids of nitrogen, and solid particles held in suspension.

**Vapor of Water.**—Atmospheric moisture is either visible, as in fogs and clouds, when it is in the form of a finely divided liquid; or invisible, as vapor of water. The amount of $H_2O$ which a given volume of air can hold, without precipitation, varies according to the temperature and the pressure. It happens rarely that air is as highly charged with moisture as it is capable of being for the existing temperature. The **fraction of saturation**, or **hygrometric state**, or **relative humidity** of the atmosphere is the percentage of that quantity of vapor of water which the air could hold at the existing temperature and pressure which it actually does hold. Thus air with a humidity of 100 is saturated, and a diminution of temperature or of pressure would cause precipitation; but an increase of temperature or of pressure would cause a diminution of humidity. Ordinarily air contains from 66 to 70 per cent. of its possible amount of moisture. If the quantity be less than this, the air is dry, and causes a parched sensation, and the sense of "stuffiness" so common in furnace-heated houses. If it be greater, evaporation from the skin is impeded, and the air is oppressive if warm.

The actual amount of moisture in air is determined by passing a known volume through tubes filled with calcium chlorid; whose increase in weight represents the amount of $H_2O$ in the volume of air used. The humidity is determined by instruments called **hygrometers, hygroscopes** or **psychrometers.**

**Carbon Dioxid.**—The quantity of carbon dioxid in free air varies from 3 to 6 parts in 10,000 by volume. (See Carbon dioxid.)

**Ammoniacal Compounds.**—Carbonate, nitrate, and nitrite of ammonium occur in small quantity (0.1 to 6.0 parts per million of $NH_3$) in air, as products of the decomposition of nitrogenized organic substances. They are absorbed and assimilated by plants.

**Nitric and Nitrous acids**, usually in combination with ammonium, are produced either by the oxidation of combustible substances containing N, or by direct union of N and $H_2O$ during discharges of atmospheric electricity. Rain-water, falling during thunder-showers, has been found to contain as much as 3.71 per million of $HNO_3$. (See Hydrogen peroxid, p. 78).

**Sulfuric and Sulfurous acids** occur, in combination with $NH_4$, in the air over cities, and manufacturing districts, where they are produced by the oxidation of S, existing in coal and coal-gas.

**Hydrocarbons** have been detected in the air of cities, and of swampy places, in small quantities.

**Solid particles** of the most diverse nature are always present in air and become visible in a beam of sunlight. Sodium chlorid is almost always present, always in the neighborhood of salt water. Air contains myriads of germs of vegetable organisms, mould, etc., which are propagated by the transportation of these germs by air-currents.

The continued inhalation of air containing large quantities of solid particles in suspension may cause severe pulmonary disorder, by mere mechanical irritation, and apart from any poisonous quality in the substance; such is the case with the air of carpeted ball-rooms, and of the workshops of certain trades, furniture polishers, metal filers, etc.

**Compounds of Nitrogen and Hydrogen.**—Three are known: **Ammonia**, $NH_3$; **Hydrazin**, $N_2H_4$; and **Hydrazoic acid**, $N_3H$; as well as salts corresponding to two hydroxids.

**Ammonia.**—*Hydrogen nitrid*—*Volatile alkali*—$NH_3$—*Molecular weight*=17—*Sp. gr.*=0.589 *A*—*Liquefies at* —40° (—40° F.)—*Boils at* —33.7° (—28.7° F.)—*Solidifies at* —75° (—103° F.)—*A litre weighs* 0.7655 gram.

**Preparation.**—(1) By union of nascent H with N.

(2) By decomposition of organic matter containing N, either spontaneously or by destructive distillation.

(3) By heating solution of ammonium hydroxid: $NH_4HO=NH_3+H_2O$.

**Properties.**—*Physical.*—A colorless gas, having a pungent odor, and an acrid taste. It is very soluble in $H_2O$, 1 volume of which at 0° (32° F.) dissolves 1050 vols. $NH_3$, and at 15° (59° F.), 727 vols. $NH_3$. Alcohol and ether also dissolve it readily. Liquid ammonia is a colorless, mobile fluid, used in ice machines for producing artificial cold, the liquid absorbing a great amount of heat in volatilizing.

*Chemical.*—At a red heat ammonia is decomposed into a mixture of N and H, occupying double the volume of the original gas. It is similarly decomposed by the prolonged passage through it of discharges of electricity. It is not readily combustible, yet it burns in an atmosphere of O with a yellowish flame. Mixtures of $NH_3$ with O, nitrogen monoxid, or nitrogen dioxid, explode on contact with flame.

The solution of ammonia in $H_2O$ constitutes a strongly alkaline liquid, known as **aqua ammoniæ**, which is possessed of strongly basic properties. It is neutralized by acids with the formation of crystalline salts, which are also formed, without liberation of hydrogen, by direct union of gaseous $NH_3$ with acid vapors. The ammoniacal salts and the alkaline base in aqua ammoniæ are compounds of a radical, **ammonium**, $NH_4$, which forms compounds corresponding to those of

potassium or sodium. The compound formed by the union of ammonia and water is **ammonium hydroxid,** $NH_4HO$: $NH_3+H_2O=NH_4HO$; and that formed by the union of hydrochloric acid and ammonia is **ammonium chlorid,** $NH_4Cl$: $NH_3+HCl=NH_4Cl$.

A very delicate test for ammonia is Nessler's reagent. This is made by dissolving 35 gm. of potassium iodid and 13 gm. of mercuric chlorid in 800 cc. $H_2O$. A cold, saturated solution of mercuric chlorid is then added, drop by drop, until the red precipitate formed no longer redissolves on agitation; 160 gm. of potassium hydroxid are then dissolved in the liquid, which is finally made up to 1000 cc. It gives a yellow color with a mere trace of $NH_3$, and a red-brown precipitate with a larger amount.

**Hydrazin — Diamid**—$H_2N.NH_2$—is known in the form of its hydroxid, corresponding to ammonium hydroxid, in the form of its salts and in numerous organic derivatives. The sulfate is produced by the action of $H_2SO_4$ upon triazoacetic acid, and the hydroxid by decomposition of the sulfate by caustic soda. The hydroxid is an oily liquid, intensely corrosive, capable of attacking glass. It combines with acids to form well-defined salts, and precipitates many metals from solutions of their salts. It is an active poison.

**Hydrazoic Acid**—**Azoimid**—$N_3H$—is a substance recently obtained from benzoyl-azoimid, which, although containing the same elements as ammonia, is distinctly acid in character. It is a colorless liquid, boiling at 37° (98.6° F.), having a very pungent and unpleasant odor. It is extremely unstable and explodes with great violence. It reacts with metals, oxids, and hydroxids, as does hydrochloric acid, to form nitrids, which, like the free acid, are very explosive.

**Hydroxylamin**—$NH_2HO$—33.—The amins and amids (q. v.) are compounds derived from ammonia by the substitution of radicals for a part or all of its hydrogen. This substance, which is intermediate in composition between ammonia and ammonium hydroxid, may be considered as ammonia, one of whose hydrogen atoms has been replaced by the radical hydroxyl, HO. It is obtained in aqueous solution by the union of nascent hydrogen with nitrogen dioxid: $NO+H_3=NH_2HO$; or by the action of nascent hydrogen upon nitric acid: $HNO_3+3H_2=2H_2O+NH_2HO$. Hydroxylamin has been obtained in colorless, hygroscopic crystals, fusing at 33° (91.4° F.). by systematic rectification of the methyl alcohol solution under diminished pressure, and by distillation of the Zn double salt, $ZnCl_2$, $2NH_2OH$ with anilin. Its aqueous solution, which probably contains the corresponding hydroxid, $NH_3O$, HO, is strongly alkaline and behaves with regard to acids as does ammonium hydroxid solution, forming salts corresponding to those of ammonium. Thus hydroxyl-ammo-

nium chlorid, $NH_4OCl$, crystallizes in prisms or tables, fusible at 100° (212° F.), and decomposed into HCl, $H_2O$ and $NH_4Cl$ at a slightly higher temperature. It is a very powerful reducing agent.

Hydroxylammonium chlorid has been used in the treatment of cutaneous disorders. It is an actively toxic agent, converting oxyhæmoglobin into methæmoglobin.

**Compounds of Nitrogen with the Halogens.—Nitrogen Chlorid**—$NCl_3$—120.5—is formed by the action of excess of Cl upon $NH_3$ or an ammoniacal compound. It is an oily, light-yellow liquid; sp. gr. 1.653; has been distilled at 71° (159.8 F.). When heated to 96° (204.8° F.), when subjected to concussion, or when brought in contact with phosphorus, alkalies or greasy matters, it is decomposed, with a violent explosion, into one volume N and three volumes Cl.

**Nitrogen Bromid.**—$NBr_3$—254—has been obtained as a reddish-brown, syrupy liquid, very volatile, and resembling the chlorid in its properties, by the action of potassium bromid upon nitrogen chlorid.

**Nitrogen Iodid.**—$NI_3$—395—When iodin is brought in contact with ammonium hydroxid solution, a dark brown or black powder, highly explosive when dried, is formed. This substance varies in composition according to the conditions under which the action occurs; sometimes the iodid alone is formed; under other circumstances it is mixed with compounds containing N, I, and H.

**Oxids of Nitrogen.**—Five are known, forming a regular series: $N_2O$, NO, $N_2O_3$, $N_2O_4$, $N_2O_5$. Of these two, the trioxid, $N_2O_3$, and pentoxid, $N_2O_5$, are anhydrids.

**Nitrogen Monoxid.**—*Nitrous oxid—Laughing gas—Nitrogen protoxid*—$N_2O$—*Molecular weight*=44—*Sp. gr.*=1.527 *A—Fuses at* —100°(—148° *F.*)—*Boils at* —87° (—124° *F.*)—*Discovered in* 1776 *by Priestley.*

**Preparation.**—By heating ammonium nitrate: $(NH_4)NO_3=N_2O+2H_2O$. To obtain a pure product there should be no ammonium chlorid present (as an impurity of the nitrate), and the heat should be applied gradually, and not allowed to exceed 250° (482° F.), and the gas formed should be passed through wash-bottles containing sodium hydroxid and ferrous sulfate.

**Properties.**—*Physical.*—A colorless, odorless gas, having a sweetish taste; soluble in $H_2O$; more so in alcohol. Under a pressure of 30 atmospheres, at 0° (32° F.), it forms a colorless, mobile liquid which, when dissolved in carbon disulfid and evaporated *in vacuo*, produces a cold of —140° (—220° F.).

*Chemical.*—It is decomposed by a red heat and by the continuous passage of electric sparks. It is not combustible, but is, after oxygen, the best supporter of combustion known.

**Physiological.** — Although, owing to the readiness with which $N_2O$ is decomposed into its constituent elements, and the nature and relative proportions of these elements, it is capable of maintaining respiration longer than any gas except oxygen or air, an animal will live for a short time only in an atmosphere of pure nitrous oxid. When inhaled, diluted with air, it produces the effects first observed by Davy in 1799: first an exhilaration of spirits, frequently accompanied by laughter, and a tendency to muscular activity, the patient sometimes becoming aggressive; afterward there is complete anæsthesia and loss of consciousness. It has been much used, by dentists especially, as an anæsthetic in operations of short duration, and in one or two instances anæsthesia has been maintained by its use for nearly an hour.

A solution in water under pressure, containing five volumes of the gas, is sometimes used for internal administration.

**Nitrogen Dioxid.**—*Nitric oxid*—NO—*Molecular weight*=30—*Sp. gr.*=1.039 *A*—*Discovered by Hales in* 1772.

**Preparation.**—By the action of copper on moderately diluted nitric acid in the cold: $3Cu+8HNO_3=3Cu(NO_3)_2+4H_2O+2NO$; the gas being collected after displacement of air from the apparatus.

**Properties.**—A colorless gas, whose odor and taste are unknown; very sparingly soluble in $H_2O$; more soluble in alcohol. The sp. gr. of the gas has been determined at —100° (—148°F.) and has been found to be same as at the ordinary temperature. This fixes the molecular weight at 30 and gives the formula NO, which is difficult to reconcile with the theory of valence. Were the formula doubled the constitution of this gas could be thus expressed : O=N—N=O. (See Nitrogen tetroxid.)

It combines with O, when mixed with that gas or with air, to form the reddish brown nitrogen tetroxid. It is absorbed by solution of ferrous sulfate, to which it communicates a dark brown or black color. It is neither combustible nor a good supporter of combustion, although ignited C and P continue to burn in it, and the alkaline metals, when heated in it, combine with its O with incandescence.

**Nitrogen Trioxid.**—*Nitrous anhydrid*—$N_2O_3$—76—Is prepared by the direct union of nitrogen dioxid and oxygen at low temperatures, or by decomposing liquefied nitrogen tetroxid with a small quantity of $H_2O$ at a low temperature: $4NO_2+H_2O=2HNO_3+N_2O_3$. It is a dark indigo-blue liquid, which, boiling at about 0° (32° F.), is partly decomposed. It solidifies at —82° (—115.6° F.).

**Nitrogen Tetroxid.**—*Nitrogen peroxid—Hyponitric acid—Nitrous fumes*—$N_2O_4$—*Molecular weight*=92—*Boils at* 22° (71.6° *F.*)—*Solidifies at* 9° (15.8° *F.*).

**Preparation.**—(1) By mixing one volume O with two volumes NO; both dry and ice-cold.

(2) By heating perfectly dry lead nitrate, O being also produced: $2Pb(NO_3)_2=2PbO+4NO_2+O_2$.

(3) By dropping strong nitric acid upon a red-hot platinum surface.

**Properties.**—When pure and dry, it is an orange-yellow liquid at the ordinary temperature; the color being darker the higher the temperature; the gas is red-brown, but becomes colorless at about 500° (932° F.). The red fumes, which are produced when nitric acid is decomposed by starch or by a metal, consist of $N_2O_4$, mixed with $N_2O_3$. The sp. gr. of the gas varies with the temperature and pressure. Values varying from 29.23 to 39.9 have been obtained (H=1). The molecular formula, $NO_2$, calls for sp. gr. 23; $N_2O_4$ for 46. These variations are due to the fact that the gas is dissociated (p. 69) at comparatively low temperatures. The formula $N_2O_4$ has been fixed as the correct one by the method of Raoult (see p. 17). It dissolves in nitric acid, forming a dark yellow liquid, which is blue or green if $N_2O_3$ be also present. With $SO_2$ it combines to form a solid, crystalline compound, which is sometimes produced in the manufacture of $H_2SO_4$. This substance, which forms the **lead chamber crystals**, is a substituted sulfurous acid, **nitrosulfonic acid**, $NO_2SO_2OH$ (see sulfonic acids). A small quantity of $H_2O$ decomposes $N_2O_4$ into $HNO_3$ and $N_2O_3$, which latter colors it green or blue. A larger quantity of $H_2O$ decomposes it into $HNO_3$ and NO. By bases it is transformed into a mixture of nitrite and nitrate: $2NO_2+2KHO=KNO_2+KNO_3+H_2O$.

It is an energetic oxydant, for which it is largely used. With certain organic substances it does not behave as an oxydant, but becomes substituted as an univalent radical; thus with benzene it forms nitro-benzene: $C_6H_5(NO_2)$.

**Toxicology.**—The brown fumes given off during many processes, in which nitric acid is decomposed, are dangerous to life. All such operations, when carried on on a small scale, as in the laboratory, should be conducted under a hood or some other arrangement, by which the fumes are carried into the open air. When in industrial processes the volume of gas formed becomes such as to be a nuisance when discharged into the air, it should be utilized in the manufacture of $H_2SO_4$, or absorbed by $H_2O$ or an alkaline solution.

An atmosphere contaminated with brown fumes is more dangerous

than one containing Cl, as the presence of the latter is more immediately annoying. At first there is only coughing, and it is only two to four hours later that a difficulty in breathing is felt, death occurring in ten to fifteen hours. At the autopsy the lungs are found to be extensively disorganized and filled with black fluid.

Even air containing small quantities of brown fumes, if breathed for a long time, produces chronic disease of the respiratory organs. To prevent such accidents, thorough ventilation in locations where brown fumes are liable to be formed is imperative. In cases of spilling nitric acid, safety is to be sought in retreat from the apartment until the fumes have been replaced by pure air from without.

**Nitrogen Pentoxid.**—*Nitric anhydrid*—$N_2O_5$—*Molecular weight*=108—*Fuses at* 30° (86° *F.*)—*Boils at* 47° (116.6° *F.*).

**Preparation.**—(1) By decomposing dry silver nitrate with dry Cl in an apparatus entirely of glass: $4AgNO_3+2Cl_2=4AgCl+2N_2O_5+O_2$.

(2) By removing water from fuming nitric acid with phosphorus pentoxid: $6HNO_3+P_2O_5=2H_3PO_4+3N_2O_5$.

**Properties.**—Prismatic crystals at temperatures above 30° (86° F.). It is very unstable, being decomposed by a heat of 50° (122° F.); on contact with $H_2O$, with which it forms nitric acid; and even spontaneously. Most substances which combine readily with O remove that element from $N_2O_5$.

**Nitrogen Acids.**—Three are known, either free or in combination, corresponding to the three oxids containing uneven numbers of O atoms:

$N_2O+H_2O=2HNO$ —Hyponitrous acid.
$N_2O_3+H_2O=2HNO_2$—Nitrous acid.
$N_2O_5+H_2O=2HNO_3$—Nitric acid.

**Hyponitrous Acid**—HNO—31—Known only in combination. Sodium hyponitrite is formed by the action of sodium upon sodium nitrate, or nitrite: $NaNO_3+4Na+2H_2O=NaNO+4NaHO$. Silver hyponitrite is formed by reduction of sodium nitrate by nascent H and decomposition with silver nitrate.

**Nitrous Acid**—*Metanitrous acid*—$HNO_2$—47—has not been isolated, although its salts, the nitrites, are well-defined compounds: $M'NO_2$ or $M''(NO_2)_2$.

The *nitrites* occur in nature, in small quantity, in natural waters, where they result from the decomposition of nitrogenous organic substances; also in saliva. They are produced by heating the corresponding nitrate, either alone or in the presence of a readily oxidizable metal, such as lead. Solutions of the nitrites are readily decomposed

by the mineral acids, with evolution of brown fumes. They take up oxygen readily and are hence used as reducing agents. Solutions of potassium permanganate are instantly decolorized by nitrites. A mixture of thin starch paste and zinc iodid solution is colored blue by nitrites, which decompose the iodid, liberating the iodin. A solution of metaphenylendiamin, in the presence of free acid, is colored brown by very minute traces of a nitrite, the color being due to the formation of triamido-azobenzene (Bismark brown).

**Nitric Acid. Aquafortis**—*Hydrogen nitrate*—**Acidum nitricum**—U. S.; Br.—$HNO_3$—63.

**Preparation.**—(1) By the direct union of its constituent elements under the influence of electric discharges.

(2) By the decomposition of an alkaline nitrate by strong $H_2SO_4$. With moderate heat a portion of the acid is liberated. $2NaNO_3+H_2SO_4=NaHSO_4+NaNO_3+HNO_3$, and at a higher temperature the remainder is given off: $NaNO_3+NaHSO_4=Na_2SO_4+HNO_3$. This is the reaction used in the manufacture of $HNO_3$.

**Varieties.**—**Commercial**—a yellowish liquid, impure, and of two degrees of concentration: **single aquafortis**; sp. gr. about 1.25=39% $HNO_3$; and **double aquafortis**; sp. gr. about 1.4=64% $HNO_3$. **Fuming**—a reddish yellow liquid, more or less free from impurities; charged with oxids of nitrogen. Sp. gr. about 1.5. Used as an oxidizing agent. C. P.—a colorless liquid, sp. gr. 1.522, which should respond favorably to the tests given below. **Acidum nitricum**, U. S.; Br.—a colorless acid, of sp. gr. 1.42=70% $HNO_3$. **Acidum nitricum dilutum**, U. S.; Br.—the last mentioned, diluted with $H_2O$ to sp. gr. 1.059=10% $HNO_3$ (U. S.), or to sp. gr. 1.101=17.44% $HNO_3$ (Br.).

**Properties.**—*Physical.*—The pure acid is a colorless liquid: sp. gr. 1.522; boils at 86° (186.8° F.); solidifies at —40° (—40° F.); gives off white fumes in damp air; and has a strong acid taste and reaction. The sp. gr. and boiling point of dilute acids vary with the concentration. If a strong acid be distilled, the boiling-point gradually rises from 86° (186.8° F.) until it reaches 123° (253.4° F.), when it remains constant, the sp. gr. of distilled and distillate being 1.42=70% $HNO_3$. If a weak acid be taken originally the boiling point rises until it becomes stationary at the same point.

*Chemical.*—When exposed to air and light, or when strongly heated, $HNO_3$ is decomposed into $N_2O_4$; $H_2O$ and O. Nitric acid is a valuable oxydant; it converts I, P, S, C, B, and Si or their lower oxids into their highest oxids; it oxidizes and destroys most organic substances, although with some it forms products of substitution. Most of the metals dissolve in $HNO_3$ as nitrates, a portion of the

acid being at the same time decomposed into NO and $H_2O$: $4HNO_3+3Ag=3AgNO_3+NO+2H_2O$. The chemical activity of $HNO_3$ is much reduced, or even almost arrested, when the intervention of nitrous acid is prevented by the presence of carbamid. The so-called "noble metals," gold and platinum, are not dissolved by either $HNO_3$ or HCl, but dissolve as chlorids in a mixture of the two acids, called **aqua regia.** In this mixture the two acids mutually decompose each other according to the equations: $HNO_3+3HCl=2H_2O+NOCl+Cl_2$ and $2HNO_3+6HCl=4H_2O+2NOCl_2+Cl_2$ with formation of **nitrosyl chlorid,** NOCl and **bichlorid,** $NOCl_2$, and nascent Cl; the last named combining with the metal. Iron dissolves easily in dilute $HNO_3$, but if dipped into the concentrated acid, it is rendered **passive,** and does not dissolve when subsequently brought in contact with the dilute acid. This passive condition is destroyed by a temperature of 40° (104° F.) or by contact with Pt, Ag or Cu. When $HNO_3$ is decomposed by zinc or iron, or in the porous cup of a Grove battery, $N_2O_3$ and $N_2O_4$ are formed, and dissolve in the acid, which is colored dark yellow, blue or green. An acid so charged is known as **nitroso-nitric acid.** Nitric acid is monobasic.

**Impurities.**—*Oxids of nitrogen* render the acid yellow, and decolorize potassium permanganate when added to the dilute acid. *Sulfuric acid* produces cloudiness when $BaCl_2$ is added to the acid, diluted with two volumes of $H_2O$. *Chlorin, iodin* cause a white ppt. with $AgNO_3$. *Iron* gives a red color when the diluted acid is treated with ammonium thiocyanate. *Salts* leave a fixed residue when the acid is evaporated to dryness on platinum.

**Nitrates.**—The nitrates of K and Na occur in nature. Nitrates are formed by the action of $HNO_3$ on the metals, or on their oxids or carbonates. They have the composition $M'NO_3$, $M''(NO_3)_2$ or $M'''(NO_3)_3$, except certain basic salts, such as the sesquibasic lead-nitrate, $Pb(NO_3)_2, 2PbO$. With the exception of a few basic salts, the nitrates are all soluble in water. When heated, they fuse and act as powerful oxidants. They are decomposed by $H_2SO_4$ with liberation of $HNO_3$.

**Analytical Characters.** — (1) Add an equal volume of concentrated $H_2SO_4$, cool, and float on the surface of the mixture a solution of $FeSO_4$. The lower layer becomes gradually colored brown, black or purple, beginning at the top.

(2) Boil in a test-tube a small quantity of HCl, containing enough sulfindigotic acid to communicate a blue color, add the suspected solution and boil again; the color is discharged.

(3) If acid, neutralize with KHO, evaporate to dryness, add to the residue a few drops of $H_2SO_4$ and a crystal of brucin (or some sulfanilic acid); a red color is produced.

(4) Add $H_2SO_4$ and Cu to the suspected liquid and boil, brown fumes appear (best visible by looking into the mouth of the test tube).

(5) A solution of diphenylamin in concentrated $H_2SO_4$ (.01 grm. in 100 cc.) is colored blue by nitric acid. A similar color is produced by other oxidizing agents.

(6) To 0.5 cc. nitrate solution add one drop aqueous solution of resorcinol (10%), and 1 drop HCl (15%), and float on the surface of 2 cc. concentrated $H_2SO_4$; a purple-red band.

**Toxicology.**—Although most of the nitrates are poisonous when taken internally in sufficiently large doses, their action seems to be due rather to the metal than to the acid radical. Nitric acid itself is one of the most powerful of corrosives.

Any animal tissue with which the concentrated acid comes in contact is rapidly disintegrated. A yellow stain, afterward turning to dirty brownish, or, if the action be prolonged, an eschar, is formed. When taken internally, its action is the same as upon the skin, but owing to the more immediately important function of the parts, is followed by more serious results (unless a large cutaneous surface be destroyed).

The symptoms following its ingestion are the same as those produced by the other mineral acids, except that all parts with which the acid has come in contact, including vomited shreds of mucous membrane, are colored yellow. The treatment is the same as that indicated when $H_2SO_4$ or HCl have been taken, i. e., neutralization of the corrosive by magnesia or soap, and dilution.

## PHOSPHORUS.

*Symbol*=P—*Atomic weight*=31 (O=16:31; H=1:30.74)—*Molecular weight*=124 ($P_4$)—*Sp. gr. of vapor*=4.2904 *A—Name from* φῶς *=light,* φέρω*=I bear—Discovered by Brandt in* 1669—**Phosphorus** (U. S.; Br.).

**Occurrence.**—Only in combination; in the mineral and vegetable worlds as phosphates of Ca, Mg, Al, Pb, K, Na. In the animal kingdom as phosphates of Ca, Mg, K and Na, and in organic combination.

**Preparation.**—From bone-ash, in which it occurs as tricalcic phosphate. Three parts of bone-ash are digested with 2 parts of strong $H_2SO_4$, diluted with 20 volumes $H_2O$, when insoluble calcic sulfate and the soluble monocalcic phosphate, or "superphosphate," are formed: $Ca_3(PO_4)_2+2H_2SO_4=H_4Ca(PO_4)_2+2CaSO_4$. The solution of superphosphate is filtered off and evaporated, the residue is mixed with about one-fourth its weight of powdered charcoal and

sand, and the mixture heated, first to redness, finally to a white heat, in earthenware retorts, whose beaks dip under water in suitable receivers. During the first part of the heating the monocalcic phosphate is converted into metaphosphate: $CaH_4(PO_4)_2=Ca(PO_3)_2+2H_2O$; which is in turn reduced by the charcoal, with formation of carbon monoxid and liberation of phosphorus, while the calcium is combined as silicate: $2Ca(PO_3)_2+2SiO_2+5C_2=2CaSiO_3+10CO+P_4$.

A direct electric process has, in great part, replaced the above industrially. A mixture of phosphate, carbon and flux is heated in a closed electric furnace provided with a condenser. The process is continuous and avoids the use of $H_2SO_4$.

The crude product is purified by fusion, first under a solution of bleaching powder, next under ammoniacal $H_2O$, and finally under water containing a small quantity of $H_2SO_4$ and potassium dichromate. It is then strained through leather and cast into sticks under warm $H_2O$.

**Properties.**—*Physical.*—Phosphorus is capable of existing in four allotropic forms:

(1) *Ordinary, or yellow variety*, in which it usually occurs in commerce. This is a yellowish, translucid solid, of the consistency of wax. Below 0° (32° F.) it is brittle; it fuses at 44.3° (111.7° F.); and boils at 290° (554° F.) in an atmosphere not capable of acting upon it chemically. Its vapor is colorless; sp. gr.=4.5A—65 H at 1040° (1940° F.). It volatilizes below its boiling point, and $H_2O$ boiled upon it gives off steam charged with its vapor. Exposed to air it gives off white fumes and produces ozone. It is luminous in the dark. It is insoluble in $H_2O$; sparingly soluble in alcohol, more soluble in ether; soluble in carbon disulfid, and in the fixed and volatile oils. It crystallizes on evaporation of its solutions in octahedræ or dodecahedræ. Sp. gr. 1.83 at 10° (50° F.).

(2) *White phosphorus* is formed as a white, opaque pellicle upon the surface of the ordinary variety, when this is exposed to light under aërated $H_2O$. Sp. gr, 1.515 at 15° (59° F.). When fused it reproduces ordinary phosphorus without loss of weight.

(3) *Black variety* is formed when ordinary phosphorus is heated to 70° (158° F.) and suddenly cooled.

(4) *Red variety* is produced from the ordinary by maintaining it at from 240° (464° F.) to 280° (536° F.) for two or three days, in an atmosphere of carbon dioxid; and, after cooling, washing out the unaltered yellow phosphorus with carbon disulfid. It is also formed upon the surface of the yellow variety, when it is exposed to direct sunlight.

It is a reddish, odorless, tasteless solid, which does not fume in air, nor dissolve in the solvents of the yellow variety. Sp. gr. 2.1.

Heated to 500° (932° F.)with lead, in the absence of air, it dissolves in the molten metal, from which it separates on cooling in violet-black, rhombohedral crystals, of sp. gr. 2.34. If prepared at 250° (482° F.) it fuses below that temperature, and at 260° (500° F.) is transformed into the yellow variety, which distils. The crystalline product does not fuse. It is not luminous at ordinary temperatures.

*Chemical.*—The most prominent property of P is the readiness with which it combines with O. The yellow variety ignites and burns with a bright flame if heated in air to 60° (140° F.), or if exposed in a finely-divided state to air at the ordinary temperature; with formation of $P_2O_3$; $P_2O_5$; $H_3PO_3$, or $H_3PO_4$, according as O is present in excess or not, and according as the air is dry or moist. The temperature of ignition of yellow P is so low that it must be preserved under boiled water. By directing a current of O upon it, P may be burned under $H_2O$, heated above 45° (113° F.). The red variety combines with O much less readily, and may be kept in contact with air without danger.

The luminous appearance of yellow P is said to be due to the formation of ozone. It does not occur in pure O at the ordinary temperature, nor in air under pressure, nor in the absence of moisture, nor in the presence of minute quantities of carbon disulfid, oil of turpentine, alcohol, ether, naphtha, and many gases.

Yellow phosphorus burns in Cl with formation of $PCl_3$ or $PCl_5$, according as P or Cl is present in excess. Both yellow and red varieties combine directly with Cl, Br, and I.

Phosphorus is not acted on by HCl or cold $H_2SO_4$. Hot $H_2SO_4$ oxidizes it with formation of phosphorous acid and sulfur dioxid: $P_4+6H_2SO_4=4H_3PO_3+6SO_2$. Nitric acid oxidizes it violently to phosphoric acid and nitrogen di- and tetr-oxids: $12HNO_3+P_4=4H_3PO_4+4N_2O_4+4NO$.

Phosphorus is a reducing agent. When immersed in cupric sulfate solution, it becomes covered with a coating of metallic copper. In silver nitrate solution it produces a black deposit of silver phosphid.

The principal uses of phosphorus are in making matches, rat paste and phosphor bronze.

**Toxicology.**—The red variety differs from the other allotropic forms of phosphorus in not being poisonous, probably owing to its insolubility, and in being little liable to cause injury by burning.

The burns produced by yellow phosphorus are more serious than a like destruction of cutaneous surface by other substances. A burning fragment of P adheres tenaciously to the skin, into which it burrows. One of the products of the combustion is metaphosphoric acid (q. v.) which, being absorbed, gives rise to true poisoning.

Burns by P should be washed immediately with dilute javelle water, liq. sodæ chlorinatæ, or solution of chlorid of lime. Yellow P should never be allowed to come in contact with the skin, except it be under cold water.

Yellow P is one of the most insidious of poisons. It is taken or administered usually as "ratsbane" or match-heads. The former is frequently starch paste, charged with phosphorus; the latter, in the ordinary sulfur match, a mixture of potassium chlorate, very fine sand, phosphorus, and a coloring matter. The symptoms in acute phosphorus-poisoning appear with greater or less rapidity, according to the dose, and the presence or absence in the stomach of substances which favor its absorption. Their appearance may be delayed for days, but as a rule they appear within a few hours. A disagreeable garlicky taste in the mouth, and heat in the stomach are first observed, the latter gradually developing into a burning pain, accompanied by vomiting of dark-colored matter, which, when shaken in the dark, is phosphorescent; low temperature and dilatation of the pupils. In some cases, death follows at this point suddenly, without the appearance of any further marked symptoms. Usually, however, the patient rallies, seems to be doing well, until, suddenly, jaundice makes its appearance, accompanied by retention of urine, and frequently delirium, followed by coma and death.

There is no known chemical antidote to phosphorus. The treatment is, therefore, limited to the removal of the unabsorbed portions of the poison by the action of an emetic, zinc or copper sulfate, or apomorphin, as expeditiously as possible, and the administration of French oil of turpentine—the older the oil the better—as a physiological antidote. The use of fixed oils or fats is to be avoided, as they favor the absorption of the poison, by their solvent action. The prognosis is very unfavorable.

**Analysis.**—When, after a death supposed to be caused by phosphorus, chemical evidence of the existence of the poison in the body, etc., is desired, the investigation must be made as soon after death as possible, for the reason that the element is rapidly oxidized, and the detection of the higher stages of oxidation of phosphorus is of no value as evidence of the administration of the element, because they are normal constituents of the body and of the food.

The detection of elementary phosphorus in a systematic toxicological analysis is connected with that of prussic acid, alcohol, ether, chloroform, and other volatile poisons. The substances under examination are diluted with $H_2O$, acidulated with tartaric acid and heated over a sand-bath in the flask *a* (Fig. 24). This flask is connected with a $CO_2$ generator, *c*, whose stopcock is closed, and with a Liebig's condenser, *e*, which is in darkness (the operation is best

conducted in a dark room), and so placed as to deliver the distillate into the flask, *f*. The odor of the distillate is noted. In the presence of P it is usually alliaceous. The condenser is also observed. If, at the point of greatest condensation, a luminous ring be observed (in the absence of *all* reflections), it is proof positive of the presence of unoxidized phosphorus. The absence, however, of that poison is not

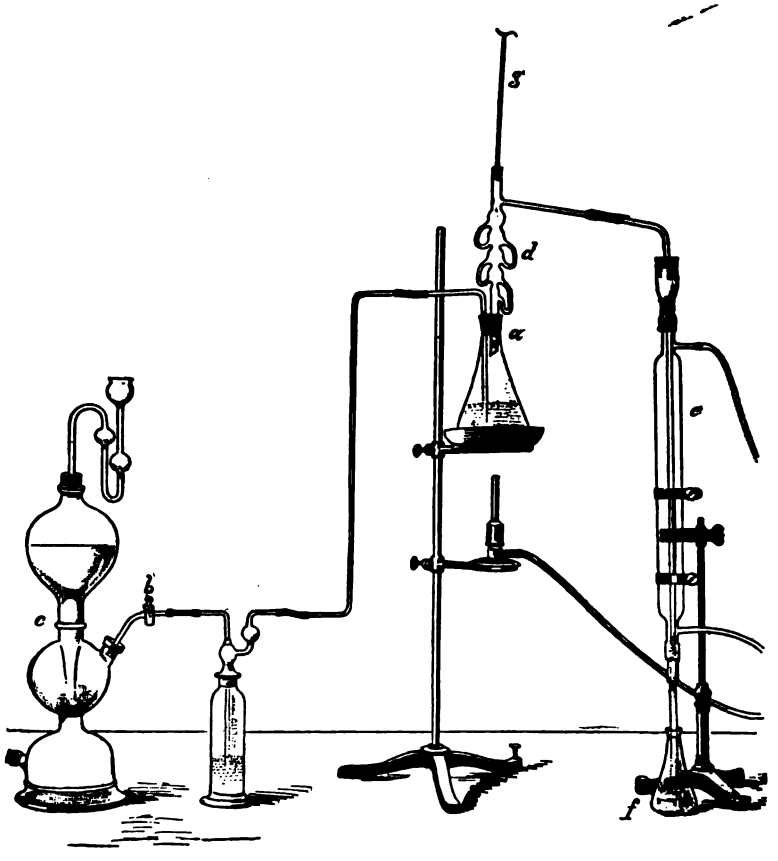



FIG. 24.

to be inferred from the absence of the luminous ring (see above). If this fail to appear, when one-third the fluid contents of the flask *a* have distilled over, the condenser is disconnected, and in its place the absorbing apparatus, Fig. 25, partly filled with a neutral solution of silver nitrate, is adjusted by a rubber tube, and a slow and constant stream of $CO_2$ is caused to traverse the apparatus from *c* (Fig. 24). If, during continuation of the distillation, no black deposit be formed in the silver solution, the absence of P may be

inferred. If a black deposit be formed, it must be further examined to determine if it be silver phosphid. For this purpose the apparatus shown in Fig. 26 is used. In the bottle *a* hydrogen is generated from *pure* Zn and $H_2SO_4$, the gas passing through the drying-tube *b*, filled with fragments of $CaCl_2$, and out through the platinum tip at *c; d* and *e* are pinch-cocks. When the apparatus is filled with H, *d* is closed until the funnel-tube *f* is three-quarters filled with the liquid from *a ;* then *e* is closed and *d* opened, and the black silver deposit, which has been collected on a filter and washed, is thrown into *f; e* is then slightly opened and the escaping gas ignited at *c*, the size of the flame being regulated by *e*. If the deposit contain P, the flame will have a green color; and, when examined with the spectroscope, will give the spectrum of bright bands shown in Fig. 27.

FIG. 25.

*Chronic phosphorus poisoning*, or *Lucifer disease*, occurs among operatives engaged in the dipping, drying, and packing of phosphorus matches. Those engaged in the manufacture of phosphorus itself are not so affected. Sickly women and children are most subject to it. The cause of the disease has been ascribed to the presence of arsenic, and to the formation of oxids of phosphorus, and of ozone. The progress of the disorder is slow, and its culminating manifestation is the destruction of one or both maxillæ by necrosis.

FIG. 26.

The frequency of the disease may be in some degree diminished by thorough ventilation of the shops, by frequent washing of the face and mouth with a weak solution of sodium carbonate, by exposing oil of turpentine in saucers in the workshops, and particularly by keeping the teeth in repair. None of these methods, however, effect a perfect prevention, which can only be attained by the substitution of the red variety of phosphorus for the yellow in this industry.

**Hydrogen Phosphids.**—Gaseous hydrogen phosphid—Phosphin—*Phosphonia*, *Phosphamin*, $PH_3$—34—a colorless gas, having a strong alliaceous odor, which is obtained pure by decomposing phosphonium iodid, $PH_4I$, with $H_2O$. Mixed with H and vapor of $P_2H_4$, it is produced, as a spontaneously inflammable gas, by the action of hot, concentrated solution of potassium hydroxid on P, or by decomposition of calcium phosphid by $H_2O$. It is highly poisonous. After death, the blood is found to be of a dark violet color, and also to have, in a great measure, lost its power of absorbing oxygen.

**Liquid hydrogen phosphid**—$P_2H_4$—66—is the substance whose vapor communicates to $PH_3$ its property of igniting on contact with air. It is separated by passing the spontaneously inflammable $PH_3$ through a bulb tube, surrounded by a freezing mixture.

FIG. 27.

It is a colorless, heavy liquid, which is decomposed by exposure to sunlight, or to a temperature of 30° (86° F.).

**Solid hydrogen phosphid**—$P_4H_2$—126—is a yellow solid, formed when $P_2H_4$ is decomposed by sunlight. It is not phosphorescent and only ignites at 160° (320° F.).

**Compounds of Phosphorus with the Halogens**—**Phosphorus Trichlorid**—$PCl_3$—137.5—is obtained by heating P in a limited supply of Cl. It is a colorless liquid; sp. gr. 1.61; has an irritating odor; fumes in air; boils at 76° (169° F.). Water decomposes it with formation of $H_3PO_3$ and HCl.

**Phosphorus Pentachlorid**—$PCl_5$—208.5—is formed when P is burnt in excess of Cl. It is a light yellow, crystalline solid: gives off irritating fumes; and is decomposed by $H_2O$.

**Phosphorus Oxychlorid**—$POCl_3$—153.5—is formed by the action of a limited quantity of $H_2O$ on the pentachlorid: $PCl_5+H_2O=POCl_3+2HCl$. It is a colorless liquid: sp. gr. 1.07; boils at 110° (230° F); and solidifies at −10° (+14° F.).

With **bromin** P forms compounds similar in composition and properties to the chlorin compounds. With **iodin** it forms two compounds, $P_2I_4$ and $PI_3$. With **fluorin** it forms two compounds, $PF_3$ and $PF_5$, the former liquid, the second gaseous.

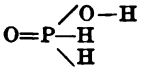
**Oxids of Phosphorus.**—Two are known: $P_2O_3$ and $P_2O_5$.

**Phosphorus Trioxid.**—*Phosphorous anhybrid, Phosphorous oxid*—$P_2O_3$—110—is formed when P is burned in a very limited supply of perfectly dry air, or O. It is white, flocculent solid, which, on exposure to air, ignites by the heat developed by its union with $H_2O$ to form phosphorous acid.

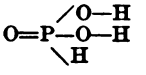
**Phosphorus Pentoxid.**—*Phosphoric anhydrid, Phosphoric oxid.*—$P_2O_5$—142—is formed when P is burned in an excess of dry O. It is a white, flocculent solid, which has almost as great a tendency to combine with $H_2O$ as has $P_2O_3$. It absorbs moisture rapidly, deliquescing to a highly acid liquid, containing, not phosphoric, but metaphosphoric acid. It is used as a drying agent.

**Phosphorus Acids.**—Six oxyacids of phosphorus are known:

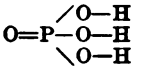
Hypophosphorous acid:



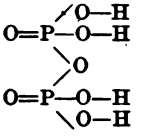
Phosphorous acid:



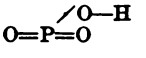
Phosphoric acid:



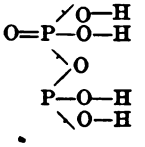
Pyrophosphoric acid:



Metaphosphoric acid:



Hypophosphoric acid:



Only those H atoms which are connected with the P atoms through O atoms are basic. Hence $H_3PO_2$ is monobasic; $H_3PO_3$ is dibasic; $H_3PO_4$ is tribasic; $H_4P_2O_7$ is tetrabasic; $HPO_2$ is monobasic, and $H_4P_2O_6$ is tetrabasic. Pyrophosphorous acid, $O{=}P_2{\equiv}(OH)_4$ is only known in an organic derivative, acetyl-pyrophosphorous acid: $O{=}P_2{\equiv}H.O(C_2H_3O).(OH)_2$; and metaphosphorous acid, $O{=}P{\equiv}O.OH$ is unknown.

**Hypophosphorous Acid.**—$H_3PO_2$—66—is a crystalline solid, or, more usually, a strongly acid, colorless syrup. It is oxidized by air to a mixture of $H_3PO_3$ and $H_3PO_4$.

**The hypophosphites**, as well as the free acid, are powerful reducing agents.

**Phosphorous Acid**—$H_3PO_3$—82—is formed by decomposition of phosphorus trichlorid by water: $PCl_3+3H_2O=H_3PO_3+3HCl$. It is a highly acid syrup, is decomposed by heat, and is a strong reducing agent.

**Phosphoric Acid**—*Orthophosphoric acid*—*Common or tribasic phosphoric acid*—**Acidum phosphoricum** (U. S.; Br.)—$H_3PO_4$—98—does not occur free in nature, but is widely disseminated in combination, in the phosphates, in the three kingdoms of nature.

It is prepared: (1) By converting bone phosphate, $Ca_3(PO_4)_2$ into the corresponding lead or barium salt, $Pb_3(PO_4)_2$ or $Ba_3(PO_4)_2$, and decomposing the former by $H_2S$, or the latter by $H_2SO_4$. (2) By oxidizing P by dilute $HNO_3$, aided by heat. The operation should be conducted with caution, and heat gradually applied by the sand bath. It is best to use red phosphorus. This is the process directed by the U. S. and Br. Pharm.

The concentrated acid is a colorless, transparent, syrupy liquid; still containing $H_2O$, which it gives off on exposure over $H_2SO_4$, leaving the pure acid, in transparent, deliquescent, prismatic crystals. It is decomposed by heat to form, first, pyrophosphoric acid, then metaphosphoric acid. It is tribasic.

If made from arsenical phosphorus, and commercial phosphorus is arsenical unless made by the electrolytic method (p. 113), it is contaminated with arsenic acid, whose presence may be recognized by Marsh's test (q. v.). The acid should not respond to the indigo and ferrous sulfate tests for $HNO_3$.

**Ortho-acids** are those in which the number of hydroxyls equals the valence of the acidulous elements. Thus orthophosphoric acid is $P(OH)_5$; orthocarbonic acid, $C(OH)_4$. Sometimes, as in the case of phosphorus, when this acid is not known, that in which the number of hydroxyls most nearly equals the valence of the acidulous element is, improperly, called the ortho-acid.

**Phosphates.**—Phosphoric acid being tribasic, the phosphates have the composition $M'H_2PO_4$; $M'_2HPO_4$; $M'_3PO_4$; $M''(H_2PO_4)_2$; $M''_2(HPO_4)_2$; $M''_3(PO_4)_2$; $M''M'PO_4$; and $M'''PO_4$. The monometallic salts are all soluble and are strongly acid. Of the dimetallic salts, those of the alkali metals only are soluble and their solutions are faintly alkaline; the others are unstable, and exhibit a marked tendency to transformation into monometallic or trimetallic salts. The normal phosphates of the alkali metals are the only soluble trimetallic phosphates. Their solutions are strongly alkaline, and they are decomposed even by weak acids:

| $Na_3PO_4$ | + | $CO_3H_2$ | = | $HNa_2PO_4$ | + | $HNaCO_3$ |
|---|---|---|---|---|---|---|
| Trisodic phosphate. | | Carbonic acid. | | Disodic phosphate. | | Monosodic carbonate. |

All the monometallic phosphates, except those of the alkali metals, are decomposed by ammonium hydroxid, with precipitation of the corresponding trimetallic salt.

**Analytical Characters.**—(1) With ammoniacal solution of silver nitrate, a yellow precipitate. (2) With solution of ammonium molybdate in $HNO_3$, a yellow precipitate. (3) With magnesia mixture,* a white, crystalline precipitate, soluble in acids, insoluble in ammonium hydroxid.

**Pyrophosphoric Acid**—$H_4P_2O_7$—178.—When phosphoric acid (or hydro-disodic phosphate) is maintained at 213° (415.4° F.), two of its molecules unite, with the loss of the elements of a molecule of water: $2H_3PO_4=H_4P_2O_7+H_2O$, to form pyrophosphoric acid.

**Metaphosphoric Acid**—*Glacial phosphoric acid*—$HPO_3$—80—is formed by heating $H_3PO_4$ or $H_4P_2O_7$ to near redness: $H_3PO_4=HPO_3+H_2O$; or $H_4P_2O_7=2HPO_3+H_2O$. It is usually obtained from bone phosphate; this is first converted into ammonium phosphate, which is then subjected to a red heat.

It is a white, glassy, transparent solid, odorless and acid in taste and reaction. Slowly deliquescent in air, it is very soluble in $H_2O$, although the solution takes place slowly, and is accompanied by a peculiar crackling sound. In constitution and basicity it resembles $HNO_3$.

The metaphosphates are capable of existing in five polymeric modifications (see polymerism): Mono- di- tri- tetra- and hexmeta- phosphates: $M'PO_3$; $M'_2(PO_3)_2$ and $M''(PO_3)_2$; $M'_3(PO_3)_3$; $M'_4(PO_3)_4$ and $M''_2(PO_3)_4$; and $M'_6(PO_3)_6$.

**Hypophosphoric Acid**—$H_4P_2O_6$—162.—When phosphorus is exposed to moist air a strongly acid liquid is slowly formed, known as **phosphatic acid.** This is a mixture of phosphorous, phosphoric and hypophosphoric acids. The last named is separated from the others by taking advantage of the sparing solubility of its acid sodium salt; this is then converted into the lead salt, which is decomposed by $H_2S$, and the liberated acid concentrated. It has not been crystallized. It is quite stable at the ordinary temperature, but slowly decomposes to a mixture of phosphorous and pyrophosphoric acids. It is quadribasic. It may be considered as formed by the union of a molecule of phosphoric acid and one of phosphorous acid, with loss of $H_2O$: $H_3PO_4+H_3PO_3=H_4P_2O_6+H_2O$.

**Action of the Phosphates on the Economy.**—The salts of phos-

* Made by dissolving 11 pts. crystallized magnesium chlorid and 28 pts. ammonium chlorid in 130 pts. water, adding 70 pts. dilute ammonium hydroxid (sp. gr. 0.96) and filtering after two days.

phoric acid are important constituents of animal tissues, and give rise, when taken internally, in reasonable doses, to no untoward symptoms. The acid itself may act deleteriously, by virtue of its acid reaction. Meta- and pyrophosphoric acids, even when taken in the form of neutral salts, have a distinct action (the pyro being the more active) upon the motor ganglia of the heart, producing diminution of the blood-pressure, and, in comparatively small doses, death from cessation of the heart's action.

## ARSENIC.

*Symbol*=As—*Atomic weight*=75 (O=16:75; H=1:74.4)—*Molecular weight*=300 ($As_4$)—*Sp. gr. of solid; crystalline*=5.75, *amorphous*=4.71; *of vapor*=10.6 *A at* 860° (1580° F.)—*Name from* ἀρσενικόν=*orpiment.*

**Occurrence.**—Free in small quantity; in combination as arsenids of Fe, Co, and Ni, but most abundantly in the sulfids, orpiment and realgar, and in arsenical iron pyrites, or mispickel.

**Preparation.**—(1) By heating mispickel in clay cylinders, which communicate with sheet iron condensing tubes.

(2) By heating a mixture of arsenic trioxid and charcoal; and purifying the product by resublimation.

**Properties.**—*Physical.*—A brittle, crystalline, steel-gray solid, having a metallic luster, or a dull, black, amorphous powder. At the ordinary pressure, and without contact of air, it volatilizes without fusion at 180° (356° F.); under strong pressure it fuses at a dull red heat. Its vapor is yellowish, and has the odor of garlic. It is insoluble in $H_2O$, and in other liquids unless chemically altered.

*Chemical.*—Heated in air it is converted into the trioxid, and ignites somewhat below a red heat. In O it burns with a brilliant, bluish-white light. In dry air it is not altered, but in the presence of moisture its surface becomes tarnished by oxidation. In $H_2O$ it is slowly oxidized, a portion of the oxid dissolving in the water. It combines readily with Cl, Br, I, and S, and with most of the metals. With H it only combines when that element is in the nascent state. Warm, concentrated $H_2SO_4$ is decomposed by As, with formation of $SO_2$, $As_2O_3$, and $H_2O$. Nitric acid is readily decomposed, giving up its O to the formation of arsenic acid. With hot HCl, arsenic trichlorid is formed. When fused with potassium hydroxid, arsenic is oxidized, H is given off, and a mixture of potassium arsenite and arsenid remains, which by greater heat is converted into arsenic, which volatilizes, and potassium arsenate, which remains.

Elementary arsenic enters into the composition of fly poison and of

shot, and is used in the manufacture of certain pigments and fireworks.

**Compounds of Arsenic and Hydrogen.**—Two are known: the solid $As_2H$ (?) and the gaseous, $AsH_3$.

**Hydrogen Arsenid—Arsin**—*Arseniuretted or arsenetted hydrogen—Arsenia—Arsenamin*—$AsH_3$—*Molecular weight*=78—*Sp. gr.*=2.695 *A—Liquefies at* —40° (—40° F.).

**Formation.**—(1) By the action of $H_2O$ upon an alloy, obtained by fusing together native sulfid of antimony, 2 pts.; cream of tartar, 2 pts.; and arsenic trioxid, 1 pt.

(2) By the action of dilute HCl or $H_2SO_4$ upon the arsenids of Zn and Sn. This is practically the same as 3, nascent hydrogen being formed by the action of the metal upon the acid.

(3) Whenever a reducible compound of arsenic is in presence of nascent hydrogen. (See Marsh test.)

(4) By the action of $H_2O$ upon the arsenids of the alkali metals.

(5) By the combined action of air, moisture and organic matter upon arsenical pigments.

(6) By the action of hot solution of potassium hydroxid upon reducible compounds of As in the presence of zinc.

**Properties.**—*Physical.*—A colorless gas; having a strong alliaceous odor; soluble in 5 vols. of $H_2O$, free from air.

*Chemical.*—It is neutral in reaction. In contact with air and moisture its H is slowly removed by oxidation, and elementary As deposited. It is also decomposed into its elements by the passage through it of luminous electric discharges; and when subjected to a red heat. It is acted on by dry O at ordinary temperatures with the formation of a black deposit, which is at first solid hydrogen arsenid, later elementary As. A mixture of $AsH_3$ and O, containing 3 vols. O and 2 vols. $AsH_3$, explodes when heated, forming $As_2O_3$ and $H_2O$. If the proportion of O be less, elementary As is deposited.

The gas burns with a greenish flame, from which a white cloud of arsenic trioxid arises. A cold surface, held above the flame, becomes coated with a white, crystalline deposit of the oxid. If the flame be cooled, by the introduction of a cold surface into it, the H alone is oxidized, and elementary As is deposited. Chlorin decomposes the gas explosively, with formation of HCl and arsenic, or arsenic trichlorid, if the Cl be in excess. In the presence of $H_2O$, arsenous and arsenic acids are formed. Bromin and iodin behave similarly, but with less violence.

All oxidizing agents decompose it readily; $H_2O$ and arsenic trioxid being formed by the less active oxidants, and $H_2O$ and arsenic acid by the more active. Solid potassium hydroxid decomposes the

gas partially, and becomes coated with a dark deposit, which seems to be elementary arsenic. Solutions of the alkaline hydroxids absorb and decompose it; H is given off and an alkaline arsenite remains in the solution. Many metals, when heated in $H_3As$, decompose it with formation of a metallic arsenid and liberation of hydrogen. Solution of silver nitrate is reduced by it; elementary silver is deposited, and the solution contains silver arsenite.

Although $H_2S$ and $H_3As$ decompose each other to a great extent, with formation of arsenic trisulfid, in the presence of air, the two gases do not act upon each other at the ordinary temperature, even in the direct sunlight, either dry or in the presence of $H_2O$, when air is absent. Hence in making $H_2S$ for use in toxicological analysis, materials free from As must be used; or the $H_2S$ must be purified as described on p. 92.

**Compounds of Arsenic with the Halogens.—Arsenic Trifluorid**—$AsF_3$—132.—A colorless, fuming liquid, boiling at 63° (145° F.), obtained by distilling a mixture of $As_2O_3$, $H_2SO_4$, and fluorspar. It attacks glass.

**Arsenic Trichlorid**—$AsCl_3$—181.5.—Obtained by distilling a mixture of $As_2O_3$, $H_2SO_4$, and NaCl, using a well-cooled receiver.

It is a colorless liquid, boils at 134° (273° F.), fumes when exposed to the air, and volatilizes readily at temperatures below its boiling point. Its formation must be avoided in processes for the chemico-legal detection of arsenic, lest it be volatilized and lost. It is formed by the action of HCl, even when comparatively dilute, upon $As_2O_3$ at the temperature of the water-bath; but, if potassium chlorate be added, the trioxid is oxidized to arsenic acid, and the formation of the chlorid thus prevented. Arsenic trioxid, when fused with sodium nitrate, is converted into sodium arsenate, which is not volatile. If, however, small quantities of chlorids be present, $AsCl_3$ is formed. It is highly poisonous.

**Arsenic Tribromid**—$AsBr_3$—315.—Obtained by adding powdered As to Br, and distilling the product at 220° (428° F.). A solid, colorless, crystalline body, fuses at 20°–25° (68°–77° F.), boils at 220° (428° F.), and is decomposed by $H_2O$.

**Arsenic Triiodid—Arsenii iodidum, U. S.**—$AsI_3$—456.—Formed by adding As to a solution of I in carbon disulfid, or by fusing together As and I in proper proportions. A brick-red solid, fusible and volatile. Soluble in a large quantity of $H_2O$. Decomposed by a small quantity of $H_2O$ into HI, $As_2O_3$, $H_2O$ and a residue of $AsI_3$.

**Compounds of Arsenic and Oxygen.**—Two are known: $As_2O_3$ and $As_2O_5$.

Probably the gray substance formed by the action of moist air on elementary arsenic is a lower oxid.

**Arsenic Trioxid** — *Arsenous anhydrid* — *Arsenous oxid* — *White arsenic*—*Arsenic*—*Arsenous acid*—**Acidum arseniosum**, U. S.; Br. —$As_2O_3$—198.

**Preparation.**—(1) By roasting the native sulfids of arsenic in a current of air.

(2) By burning arsenic in air or oxygen.

**Properties.**—*Physical.*—It occurs in three forms: *crystallized* or "*powdered*," *vitreous*, and *porcelainous*. When freshly fused, it appears in colorless or faintly yellow, translucent, vitreous masses, having no visible crystalline structure. Shortly, however, these masses become opaque upon the surface, and present the appearance of porcelain. This change slowly progresses toward the center of the mass, which, however, remains vitreous for a long time. When arsenic trioxid is sublimed, if the vapors be condensed upon a cool surface, it is deposited in the form of brilliant octahedral crystals, which are larger and more perfect the nearer the temperature of the condensing surface is to 180° (356° F.). When sublimed under slightly increased pressure, or in an atmosphere of $SO_2$, right rhombic prisms occur among the octahedra. It is therefore dimorphous. The crystalline variety may be converted into the vitreous, by keeping it for some time at a temperature near its point of volatilization.

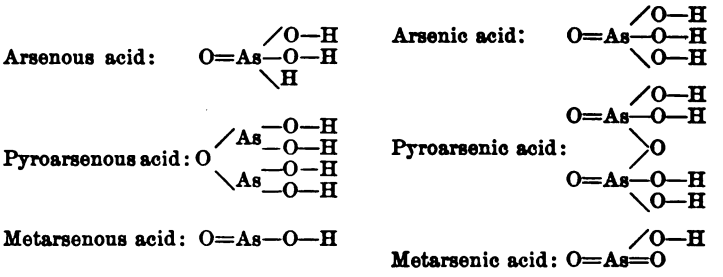
Although $As_2O_3$ is heavier than water, when thrown upon that liquid a large part of the crystalline powder floats, and a part of that which sinks at first subsequently rises. This is due to adhesion of air to the particles of the solid. The same phenomenon renders the solution of $As_2O_3$ in water slow and irregular. The vitreous variety is more readily soluble than the crystalline. The taste of arsenic trioxid in solution is very faint, at first sweetish, afterward very slightly metallic. The solid is almost tasteless. It is odorless. In aqueous solution it has a faintly acid reaction. The sp. gr. of the vitreous variety is 3.785; that of the crystalline, 3.689.

*Chemical.*—Its solutions are acid in reaction, and probably contain the true arsenous acid, $H_3AsO_3$. They are neutralized by bases, with formation of **arsenites.** Solutions of sodium, or potassium hydroxid, or carbonate dissolve it, with formation of the corresponding arsenite. It is readily reduced, with separation of As, when heated with hydrogen, carbon, and potassium cyanid, and at lower temperatures by more active reducing agents. Oxidizing agents, such as $HNO_3$, the chlorin oxyacids, chromic acid, convert it into arsenic pentoxid or arsenic acid. Its solution, acidulated with HCl and boiled in presence of copper, deposits on the metal a gray film, composed of an alloy of Cu and As.

**Arsenic Pentoxid**—*Arsenic anhydrid*—*Arsenic oxid*—$As_2O_5$—230—is obtained by heating arsenic acid to redness. It is a white, amor-

phous solid, which, when exposed to the air, slowly absorbs moisture. It is fusible at a dull red heat, and at a slightly higher temperature decomposes to $As_2O_3$ and O. It dissolves slowly in $H_2O$, forming arsenic acid, $H_3AsO_4$.

**Arsenic Acids.**—The oxyacids of arsenic form a series, corresponding to that of the oxyacids of phosphorus, except that the hypoarsenous and hypoarsenic acids are unknown, and pyro- and metarsenous acids are known in their salts:




**Arsenous Acid.**—$H_3AsO_3$—126—exists in aqueous solutions of the trioxid, although it has not been separated. Corresponding to it are important salts, called **arsenites**, which have the general formulæ $HM'_2AsO_3$, $HM''AsO_3$, $H_4M''(AsO_3)_2$. Pyro- and metarsenous acids are only known in combination.

**Arsenic Acid**—*Orthoarsenic acid*—$H_3AsO_4$—142—is obtained by oxidizing $As_2O_3$ with $HNO_3$ in the presence of $H_2O$: $As_2O_3+2H_2O+2HNO_3=2H_3AsO_4+N_2O_3$. A similar oxidation is also effected by Cl, aqua regia, and other oxidants.

A syrupy, colorless, strongly acid solution is thus obtained, which, at 15° (59° F.), becomes semi-solid, from the formation of transparent crystals, containing 1 Aq. These crystals, which are very soluble and deliquescent, lose their Aq at 100° (212° F.), and form a white, pasty mass, composed of minute white, anhydrous needles. At higher temperatures it is converted into $H_4As_2O_7$, $HAsO_3$, and $As_2O_5$. In presence of nascent H it is decomposed into $H_2O$ and $AsH_3$. It is reducible to $H_3AsO_3$ by $SO_2$.

The action of $H_2S$ upon acid solutions of arsenic acid, or of the arsenates, varies with the rapidity of the action and the temperature at which it occurs. With a slow current of $H_2S$, at a low temperature, no precipitate is formed, and the solution remains colorless. Under these conditions **thioxyarsenic acid**, $H_3AsO_3S$, is formed: $H_3AsO_4+H_2S=H_3AsSO_3+H_2O$. By a further action of $H_2S$, arsenic pentasulfid is formed: $2H_3AsO_3S+3H_2S=As_2S_5+6H_2O$. If the current of $H_2S$ be very slow, the thioxyarsenic acid produced is decomposed according to the equation: $2H_3AsO_3S=As_2O_3+3H_2O+S_2$ and

the precipitate then produced consists of a mixture of $As_2S_3$, $As_2S_5$ and S.

Like phosphoric acid, arsenic acid is tribasic; and the arsenates resemble the phosphates in composition, and in many of their chemical and physical properties.

**Pyroarsenic Acid**—$H_4As_2O_7$—266.—Arsenic acid, when heated to 160° (320°F.), is converted into compact masses of pyroarsenic acid: $2H_3AsO_4=H_4As_2O_7+H_2O$. It is very prone to revert to arsenic acid, by taking up water.

**Metarsenic Acid**—$HAsO_3$—124.—At 200°–206° (392°–403° F.) $H_4As_2O_7$ gradually loses $H_2O$ to form metarsenic acid: $H_4As_2O_7=2HAsO_3+H_2O$. It forms white, pearly crystals, which dissolve readily in $H_2O$, with regeneration of $H_3AsO_4$. It is monobasic.

**Compounds of Arsenic and Sulfur.—Arsenic Disulfid**—*Red sulfid of arsenic—Realgar—Red orpiment—Ruby sulfur—Sandarach*—$As_2S_2$—214—occurs in nature, in translucent, ruby-red crystals. It is also prepared by heating a mixture of $As_2O_3$ and S. As so obtained it appears in brick-red masses.

It is fusible, insoluble in $H_2O$, but soluble in solutions of the alkaline sulfids, and in boiling solution of potassium hydroxid.

**Arsenic trisulfid**—*Orpiment—Auripigmentum—Yellow sulfid of arsenic—King's yellow*—$As_2S_3$—246—occurs in nature in brilliant golden yellow flakes. Obtained by passing $H_2S$ through an acid solution of $As_2O_3$; or by heating a mixture of As and S, or of $As_2O_3$ and S in equivalent proportions.

When formed by precipitation, it is a lemon-yellow powder; or in orange-yellow, crystalline masses, when prepared by sublimation. Almost insoluble in cold $H_2O$, but sufficiently soluble in hot $H_2O$ to communicate to it a distinct yellow color. By continued boiling with $H_2O$ it is decomposed into $H_2S$ and $As_2O_3$. Insoluble in dilute HCl; but readily soluble in solutions of the alkaline hydroxids, carbonates, and sulfids. It volatilizes when heated.

Nitric acid oxidizes it, forming $H_3AsO_4$ and $H_2SO_4$. A mixture of HCl and potassium chlorate has the same effect. It corresponds in constitution to $As_2O_3$, and like it, may be regarded as an anhydrid, for although thioarsenous acid, $H_3AsS_3$, has not been separated, the thioarsenites, pyro- and meta-thioarsenites are well-characterized compounds.

**Arsenic Pentasulfid**—$As_2S_5$—310—is formed by fusing a mixture of $As_2S_3$ and S in proper proportions, and, by the prolonged action of $H_2S$, at low temperatures, upon solutions of the arsenates.

It is a yellow, fusible solid, capable of sublimation in absence of air. There exist well-defined thioarsenates, pyro-and meta-thioarsenates.

### Action of Arsenical Compounds Upon the Animal Economy.

The poisonous nature of many of the arsenical compounds has been known from remote antiquity, and it is probable that more murders have been committed by their use than by that of all other toxic substances combined. Even at the present time — notwithstanding the fact that, suspicion once aroused, the detection of arsenic in the dead body is certain and comparatively easy—criminal arsenical poisoning is still quite common, especially in rural districts.

The poison is usually taken by the mouth, but it has also been introduced by other channels; the skin, either uninjured or abraded, the rectum, vagina, and male urethra. The forms in which it has been taken are: (1) **Elementary arsenic,** which is not poisonous so long as it remains such. In contact with water, or with the saliva, however, it is converted into an oxid, which is then dissolved, and, being capable of absorption, produces the characteristic effects of the arsenical compounds. Certain fly-papers and fly-poisons contain As, a portion of which has been oxidized by the action of air and moisture. (2) **Hydrogen arsenid,** the most actively poisonous of the inorganic compounds of arsenic, has been the cause of several accidental deaths, among others, that of the chemist Gehlen, who died in consequence of having inhaled the gas while experimenting with it. In other cases death has followed the inhalation of hydrogen, made from zinc and sulfuric acid contaminated with arsenic. (3) **Arsenic trioxid** is the compound most frequently used by criminals. It has been given by every channel of entrance to the circulation; in some instances concealed with great art, in others merely held in suspension by stirring in a transparent fluid, given to an intoxicated person. If the poison have been in quantity, and undissolved, it may be found in the stomach after death, in the form of eight-sided crystals, more or less worn by the action of the solvents with which it has come in contact. (4) **Potassium arsenite,** the active substance in "Fowler's solution," although largely used by the laity in malarial districts as an ague-cure, has, so far as the records show, produced but few cases of fatal poisoning. (5) **Sodium arsenite** is sometimes used to clean metal vessels, a practice whose natural results are exemplified in the death of an individual who drank beer from a pewter mug so cleaned; and in the serious illness of 340 children in an English institution, in which this material had been used for cleaning the water-boiler. (6) **Arsenic acid and arsenates.**—The acid itself has, so far as we know, been directly fatal to no one. The cases of death and illness, however, which have been put to the account of the red anilin dyes, are not due to them directly,

but to arsenical residues remaining in them as the result of defective processes of manufacture. (7) **Sulfids of arsenic.**—Poisoning by these is generally due to the use of orpiment, introduced into articles of food as a coloring matter, by a combination of fraud and stupidity, in mistake for turmeric. (8) **The arsenical greens.**—Scheele's green, or cupric arsenite, and Schweinfurth green, or cupric acetometarsenite (the latter commonly known in the United States as **Paris green**, a name applied in Europe to one of the anilin pigments). These substances, although rarely administered with murderous intent, have been the cause of death in a great number of cases.

The arsenical pigments may also produce disastrous results by "accident;" by being incorporated in ornamental pieces of confectionery; by being used in the coloring of textile fabrics, from which they may be easily rubbed off; from their use for the destruction of insects, and by being used in the manufacture of wall-paper. Many instances of chronic or subacute arsenical poisoning have resulted from inhabiting rooms hung with paper whose whites, reds, or greens were produced by arsenical pigments. From such paper the poison is disseminated in the atmosphere of the room in two ways: either as an impalpable powder, mechanically detached from the paper and floating in the air, or by their decomposition, and the consequent diffusion of volatile arsenical compounds in the air.

**The treatment** in acute arsenical poisoning is the same, whatever may be the form in which the poison has been taken, if it have been taken by the mouth. The first indication is the removal of any unabsorbed poison from the alimentary canal. If vomiting have not occurred from the effects of the toxic, it should be induced by the administration of zinc sulfate, or by mechanical means. When the stomach has been emptied, the chemical antidote is to be administered, with a view to the transformation, in the stomach, of any remaining arsenical compound into the insoluble, and therefore innocuous, ferrous arsenate. To prepare the antidote, a solution of ferric sulfate, *Liq. ferri tersulphatis* (U. S.)=*Liq. ferri persulphatis* (Br) is to be diluted with three volumes of water, and treated with aqua ammoniæ in slight excess. The precipitate formed is then collected upon a muslin filter, and washed with water until the washings are nearly tasteless. The contents of the filter—*Ferri oxidum hydratum* (U. S.), *Ferri peroxidum humidum* (Br.) are to be given moist, in repeated doses of one to two teaspoonsful, until an amount of the hydrate equal to 20 times the weight of white arsenic taken has been administered. Dialyzed iron may be given while the hydrate is in preparation, or whenever the materials for its preparation are not obtainable.

## Precautions to be taken by the Physician in cases of Suspected Poisoning.

It will rarely happen that in a case of suspected homicidal poisoning by arsenic, or by other poisons, the physician in charge will be willing or competent to conduct the chemical analysis, upon which, probably, the conviction or acquittal of the accused will mainly depend. Upon his knowledge and care, however, the success or futility of the chemist's labors depends in a great measure.

It is, as a rule, the physician who first suspects foul play; and while it is undoubtedly his duty to avoid any public manifestation of his suspicion, it is as certainly his duty toward his patient and toward the community, to satisfy himself as to the truth or falsity of his suspicion by the application of a simple test to the excreta of the patient during life, the result of which may enable him to prevent a crime, or, failing that, take the first step toward the punishment of the criminal.

In a case in which, from the symptoms, the physician suspects poisoning by any substance, he should himself test the urine or fæces, or both, and govern his treatment and his actions toward the patient, and those surrounding the patient, by the results of his examination. Should the case terminate fatally, he should at once communicate his suspicions to the prosecuting officer, and require a post-mortem investigation, which should, if at all possible, be conducted in the presence of the chemist who is to conduct the analysis. For, be the physician as skilled as he may, there are odors and appearances, observable in many cases at the opening of the body, full of meaning to the toxicological chemist, which are ephemeral, and whose bearing upon the case is not readily recognized by those not thoroughly experienced.

Cases frequently arise in which it is impossible to bring the chemist upon the ground in time for the autopsy. In such cases the physician should remember that that portion of the poison remaining in the alimentary tract (we are speaking of true poisons) is but the residue of the dose in excess of that which has been necessary to produce death; and, if the processes of elimination have been active, there may remain no trace of the poison in the alimentary canal, while it still may be detectable in the deeper-seated organs. The poison may also have been administered by another channel than the mouth, in which event it may not reach the stomach..

For these reasons it is not sufficient to send the stomach alone for analysis. The chemist should also receive the entire intestinal canal, the liver, the spleen, one or both kidneys, a piece of muscular tissue from the leg, the brain, and any urine that may remain

in the bladder. The intestinal canal should be removed and sent to the chemist *without having been opened*, and with ligatures, enclosing the contents, at the two ends of the stomach and at the lower end of the intestine. The brain and alimentary canal are to be placed in separate jars, and the other viscera in another jar together; the urine in a vial by itself. All of these vessels are to be new and clean, and are to be closed by new corks, or by glass stoppers, or covers (not zinc screw-caps), which are then coated with paraffin (not sealing-wax), and so fastened with strings and seals, that it is impossible to open the vessels without cutting the strings or breaking the seals. Any vomited matters are to be preserved. If the physician fail to observe these precautions, he has probably made the breach in the evidence through which the criminal will escape, and has at the outset defeated the aim of the analysis.

**Analytical Characters of the Arsenical Compounds.—Arsenous Compounds.**—(1) $H_2S$, a yellow color in neutral or alkaline liquids; a yellow ppt. in acid liquids. The ppt. dissolves in solutions of the alkaline hydroxids, carbonates and sulfhydrates; but is scarcely affected by HCl. Hot $HNO_3$ decomposes it.

(2) $AgNO_3$, in the presence of a little $NH_4HO$, gives a yellow ppt. This test is best applied by placing the neutral arsenical solution in a porcelain capsule, adding neutral solution of $AgNO_3$, and blowing upon it over the stopper of the $NH_4HO$ bottle, moistened with that reagent.

(3) $CuSO_4$ under the same conditions as in (2) gives a yellowish green ppt.

(4) A small quantity of solid $As_2O_3$ is placed in the point *a* of the tube, Fig. 28; above it, at *b*, a splinter of recently ignited charcoal; *b* is first heated to redness, then *a;* the vapor of $As_2O_3$, passing over the hot charcoal, is reduced, and elementary As is deposited at *c* in a metallic ring. The tube is then cut between *a* and *c*, the larger piece held with *d* uppermost and heated at *c;* the deposit is volatilized, the odor of garlic is observed, and bright, octahedral crystals (Fig. 30) appear in the cool part of the tube.

FIG. 28.

(5) **Reinsch Test.**—The suspected liquid is acidulated with one-sixth its bulk of HCl. Strips of electrotype copper are immersed in the liquid, which is boiled. In the presence of an arsenous compound, a gray or bluish deposit is formed upon the Cu. A similar

deposit is produced by other substances (S, Au, Pt, Bi, Sb, Hg). To complete the test the Cu is removed, washed, and dried between folds of filter paper, without removing the deposit. The copper, with its adherent film, is rolled into a cylinder, and introduced into a dry piece of Bohemian tubing, about one-fourth inch in diameter and six inches long, which is held at the angle shown in Fig. 29 and heated at the point containing the copper. If the deposit consist of arsenic, a white deposit is formed at *a*, which contains brilliant specks, and, when examined with a magnifier, is found to consist entirely of minute octahedral crystals (Fig. 30).

If the stain upon the copper, formed in the first part of the reaction, have been caused by S, Au, Pt, or Bi, no sublimate is produced during the subsequent heating in the glass tube, as the product of oxidation of sulfur is gaseous, Au and Pt are neither oxidized nor volatilized, and Bi is oxidized, but its oxid is not volatile. Sublimates are, however, formed from deposits caused by Sb or Hg, which

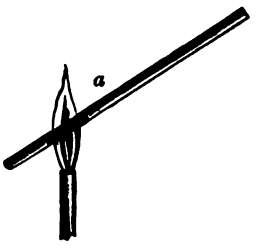



FIG. 29.

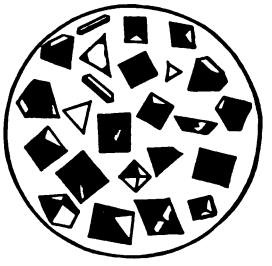


FIG. 30.

differ from that produced by arsenic in the following respects: That from Sb consists of $Sb_2O_3$, which, although isodimorphous with $As_2O_3$, does not crystallize under these conditions, except, sometimes, to form prismatic crystals *at* the heated part of the tube, or an occasional octahedral crystal beyond. The sublimate is entirely, or almost entirely amorphous, or granular, possibly containing one or two octahedral crystals, whose borders are darker than those of $As_2O_3$. The sublimate from Hg consists of microscopic globules of the liquid metal. Reinsch's reaction is, therefore, a test for antimony and mercury, as well as for arsenic.

The advantages of this test are: it may be applied in the presence of organic matter, to the urine for instance; it is easily conducted; and its positive results are not misleading, *if the test be carried to completion*. These advantages render it the most suitable method for the physician to use, *during the life of the patient*. It should not be used *after death* by the physician, as by it copper is introduced into the substances under examination, which may subsequently interfere seriously with the analysis. The purity of the Cu and HCl must be

proved by a blank testing before use. Reinsch's test is not as delicate as Marsh's, and it only reacts slowly and imperfectly when the arsenic is in the higher stage of oxidation, or in presence of oxidizing agents.

(6) **Marsh's test** is based upon the formation of $AsH_3$ when a reducible compound of arsenic is in presence of nascent H; and the subsequent decomposition of the arsenical gas by heat, with separation of elementary arsenic.

The apparatus used (Fig. 31) consists of a glass generating vessel, *a*, of about 150 cc. capacity, provided with a funnel-tube having a stop-cock, and a lateral outlet, either fitted in with a cork, or, better, ground in. The lateral outlet is connected with a tube, *b*, filled with fragments of calcium chlorid; which in turn connects with the

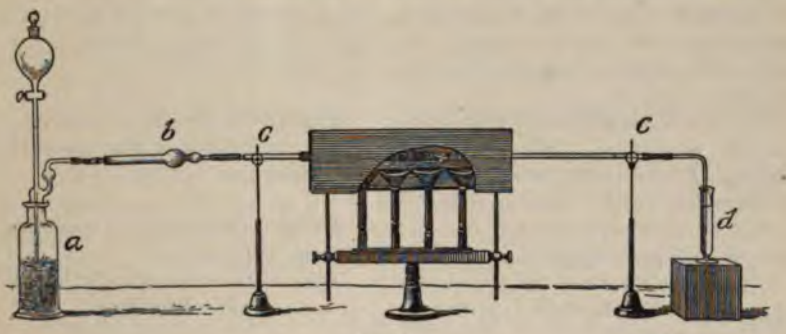



FIG. 31.

Bohemian glass tube *cc*, which should be about 0.5 cent. in diameter, and about 80 cent. long. The tube is protected by a tube of wire gauze, within which it is adjusted in the furnace as shown in the figure. The other end of *cc* is bent downward, and dips into a solution of silver nitrate in the test-tube, *d*.

The vessel *a* is first charged with about 25 grams of an alloy of pure granulated zinc, with a small quantity of platinum. The apparatus is then connected gas-tight, and the funnel tube about half filled with $H_2SO_4$, diluted with an equal bulk of $H_2O$, and cooled. By opening the stopcock, the acid is brought in contact with the zinc in small quantities, in such a manner that during the entire testing bubbles of gas pass through *d* at the rate of 60–80 per minute. After fifteen minutes the burner is lighted, and the heating continued, during evolution of gas from zinc and $H_2SO_4$, for an hour. At the end of that time, if no stain have formed in *cc* beyond the burner, the zinc and acid may be considered to be pure, and the suspected solution, which must have been previously freed from organic matter and from tin and antimony, is introduced slowly through the funnel-tube.

If arsenic be present in the substance examined, a hair-brown or gray deposit is formed in the cool part of *cc* beyond the heated part. At the same time the contents of *d* are darkened if the amount of As present is so great that all the $AsH_3$ produced is not decomposed in the heated portion of *cc*.

To distinguish the stains produced by arsenical compounds from the similar ones produced by antimony the following differences are noted :

| *The Arsenical Stain.* | *The Antimonial Stain.* |
|---|---|
| *First.* — Is farther removed from the heated portion of the tube, and, if small in quantity, is double — the first hair-brown, the second steel-gray. | *First.* — Is quite near the heated portion of the tube. A second stain is also usually formed in front of the heated part of the tube. |
| *Second.* — Volatilizes readily when heated in an atmosphere of hydrogen, being deposited farther along in the tube. The escaping gas has the odor of garlic. | *Second.* — Requires a much higher temperature for its volatilization; fuses before volatilizing. Escaping gas has no alliaceous odor. |
| *Third.* — When cautiously heated in a current of oxygen, brilliant, white, octahedral crystals of arsenic trioxid are deposited farther along in the tube. | *Third.* — No crystals formed by heating in oxygen, but an amorphous, white sublimate (see p. 132). |
| *Fourth.* — Instantly soluble in solution of sodium hypochlorite. | *Fourth.* — Insoluble in solution of sodium hypochlorite. |
| *Fifth.* — Slowly dissolved by solution of ammonium sulfhydrate ; more rapidly when warmed. | *Fifth.* — Dissolves quickly in solution of ammonium sulfhydrate. |
| *Sixth.* — The solution obtained in five leaves, on evaporation over the water-bath, a bright yellow residue. | *Sixth.* — The solution obtained in five leaves, on evaporation over the water-bath, an orange-red residue. |
| *Seventh.* — The residue obtained in six is soluble in aqua ammoniæ, but insoluble in hydrochloric acid. | *Seventh.* — The residue obtained in six is insoluble in aqua ammoniæ, but soluble in hydrochloric acid. |
| *Eighth.* — Is soluble in warm nitric acid; the solution on evaporation yields a white residue, which turns brick-red when moistened with silver nitrate solution. | *Eighth.* — Is soluble in warm nitric acid; the solution on evaporation yields a white residue, which is not colored when moistened with silver nitrate solution. |
| *Ninth.* — Is not dissolved by a solution of stannous chlorid. | *Ninth.* — Dissolves slowly in solution of stannous chlorid. |

The silver solution in *d* is tested for arsenous acid, by floating upon its surface a layer of diluted $NH_4HO$ solution, which, in the presence of arsenic, produces a yellow (not brown) band, at the point of junction of the two liquids.

In place of bending the tube *c* downward, it may be bent upward and drawn out to a fine opening. If the escaping gas be then ignited, the heating of the tube being discontinued, a white deposit of $As_2O_3$

may be collected on a glass surface held *above* the flame ; or a brown deposit of elementary As upon a cold (porcelain) surface held *in* the flame.

In place of generating nascent hydrogen by the action of Zn on $H_2SO_4$, it may be produced by the decomposition of acidulated $H_2O$ by the battery, in a Marsh apparatus especially modified for that purpose.

In another modification of the Marsh test the $AsH_3$ is decomposed, not by passage through a red-hot tube, but by passing through a tube traversed by the spark from an induction coil.

(7) **Fresenius' and Von Babo's test.** — The sulfid, obtained in (1), is dried, and mixed with 12 parts of a *dry* mixture of 3 pts. sodium carbonate and 1 pt. potassium cyanid, and the mixture brought into a tube, drawn out to a fine opening, through which a slow current of $CO_2$ is allowed to pass. The tube is then heated to redness at the point containing the mixture, when, if arsenic be present, a gray deposit is formed at the constricted portion of the tube ; which has the characters of the arsenical stain indicated on p. 134.

(8) Place a small crystal of sodium sulfite in a solution of 0.3–0.4 gram of stannous chlorid in pure HCl, sp. gr. 1.13. Float the liquid to be tested on the surface of this mixture. If As be present a yellow band is formed at the junction of the two liquids, and gradually increases upwards.

ARSENIC COMPOUNDS.—(1) $H_2S$ does not form a ppt. in neutral or alkaline solutions. In acid solutions a yellow ppt., consisting either of $As_2S_3$ or $As_2S_5$, or a mixture of the sulfids with free S, is formed only after prolonged passage of $H_2S$ at the ordinary temperature, more rapidly at about 70° (158° F.).

(2) $AgNO_3$, under the same conditions as with the arsenous compounds, produces a brick-red ppt. of silver arsenate.

(3) $CuSO_4$ under like circumstances produces a bluish green ppt.

Arsenic compounds behave like arsenous compounds with the tests 4, 6 and 7 for the latter.

**Method of Analysis for Mineral Poisons.**—In cases of suspected poisoning a systematic course of analysis is to be followed by which the presence or absence of *all* the more usual poisons can be determined. The most advantageous process for this purpose is that of Fresenius and Van Babo, somewhat modified, in which the animal and vegetable substances are disintegrated and oxidized by a mixture of HCl and $KClO_3$, and in which arsenic and antimony, if present, are separated before application of the Marsh test. For descriptions of the methods, which are somewhat intricate, the student is referred to more comprehensive works.

## ANTIMONY.

*Symbol*=Sb (*Latin: stibium*)—*Atomic weight*=120 (O=16 : 120; H=1 : 119.04)—*Molecular weight*=(?)—*Sp. gr.*=6.175—*Fuses at* 450° (842° F.).

**Occurrence.**—Free in small quantity; principally in the trisulfid, $Sb_2S_3$.

**Preparation.**—The native sulfid (black or crude antimony) is roasted, and then reduced by heating with charcoal.

**Properties.**—*Physical.*—A bluish gray, brittle solid, having a metallic luster; readily crystallizable; tasteless and odorless; volatilizes at a red heat, and may be distilled in an atmosphere of H.

*Chemical.*—Is not altered by dry or moist air at ordinary temperatures. When sufficiently heated in air, it burns, with formation of $Sb_2O_3$, as a white, crystalline solid. It also combines directly with Cl, Br, I, S, and many metallic elements. It combines with H under the same circumstances as does As. Cold dilute $H_2SO_4$ does not affect it; the hot concentrated acid forms with it antimonyl sulfate $(SbO)_2SO_4$ and $SO_2$. Hot HCl dissolves it, when finely divided, with evolution of H. It is readily oxidized by $HNO_3$, with formation of $H_3SbO_4$ or $Sb_2O_4$. Aqua regia dissolves it as $SbCl_3$, or $SbCl_5$. Solutions of the alkaline hydroxids do not act on it.

The element does not form salts with the oxyacids. There are, however, compounds, formed by the substitution of the group **antimonyl** (SbO), for the basic hydrogen of those acids. (See Tartar emetic).

It enters into the composition of type metal, anti-friction metals, and britannia metal.

**Hydrogen Antimonid—Stibin**—*Antimoniuretted hydrogen—Stibamin—Stibonia*—$SbH_3$—123.—It is produced, mixed with H, when a reducible compound of Sb is in presence of nascent H. It is obtained in larger amount by decomposing an alloy of 400 parts of a 2% sodium amalgam, and 8 parts of freshly reduced, and dried Sb, by $H_2O$, in a current of $CO_2$.

It is a colorless, odorless, combustible gas, subject to the same decompositions as $AsH_3$; from which it differs in being by no means as poisonous, and in its action upon silver nitrate solution. The arsenical gas acts upon the silver salt according to the equation: $6AgNO_3+2AsH_3+H_2=Ag_2+2Ag_2HAsO_3+6HNO_2$, and the precipitate formed is elementary silver, while $Ag_2HAsO_3$ remains in the solution. In the case of $SbH_3$ the reaction is $3AgNO_3+SbH_3=3HNO_3+SbAg_3$, all of the Sb being precipitated in the black silver antimonid.

**Chlorids of Antimony.—Antimony Trichlorid**—*Protochlorid* or *butter of antimony*—$SbCl_3$—226.5—is obtained by passing dry Cl over an excess of $Sb_2S_3$; by dissolving $Sb_2S_3$ in HCl; or by distilling mix-

tures, either of $Sb_2S_3$ and mercuric chlorid, or of Sb and mercuric chlorid, or of antimonyl pyrosulfate and sodium chlorid.

At low temperatures it is a solid, crystalline body; at the ordinary temperature a yellow, semi-solid mass, resembling butter; at 73.2° (164° F.) it fuses to a yellow, oily liquid, which boils at 223° (433.4° F.). Obtained by a solution of $Sb_2S_3$ in HCl of the usual strength, it forms a dark yellow solution, which, when concentrated to sp. gr. 1.47, constitutes the *Liq. Antimonii chloridi* (Br.).

It absorbs moisture from air, and is soluble in a small quantity of $H_2O$; with a larger quantity it is decomposed, with precipitation of a white powder, **powder of Algaroth,** whose composition is SbOCl if cold $H_2O$ be used, and $Sb_4O_5Cl_2$ if the $H_2O$ be boiling. In $H_2O$ containing 15 per cent. or more HCl, $SbCl_3$ is soluble without decomposition.

**Antimony Pentachlorid**—$SbCl_5$—297.5— is formed by the action of Cl, in excess, upon Sb or $SbCl_3$.

It is a fuming, colorless liquid. With a small quantity of $H_2O$, and by evaporation over $H_2SO_4$, it forms a hydrate, $SbCl_5 4H_2O$, which appears in transparent, deliquescent crystals. With more $H_2O$, a crystalline oxychlorid, $SbOCl_3$, is formed; and with a still greater quantity, a white precipitate of orthoantimonic acid, $H_3SbO_4$.

**Compounds of Antimony and Oxygen.**—Three are known, $Sb_2O_3$, $Sb_2O_4$ and $Sb_2O_5$.

**Antimony Trioxid**—*Antimonous anhydrid*—*Oxid of antimony*—**Antimonii oxidum** (U. S.; Br.)—$Sb_2O_3$—288—occurs in nature; and is prepared artificially by decomposing the oxychlorid; or by heating Sb in air.

It crystallizes in prisms or in octahedra, and is isodimorphous with $As_2O_3$, or is an amorphous, insoluble, tasteless, odorless powder; white at ordinary temperatures, but yellow when heated. It fuses readily, and may be distilled in absence of oxygen. Heated in air, it burns like tinder, and is converted into $Sb_2O_4$.

It is reduced, with separation of Sb, when heated with charcoal, or in H. It is also readily oxidized by $HNO_3$, or potassium permanganate. It dissolves in HCl as $SbCl_3$; in Nordhausen sulfuric acid, from which solution brilliant crystalline plates of antimonyl pyrosulfate, $(SbO)_2S_2O_7$, separate; and in solutions of tartaric acid, and of hydropotassic tartrate (see Tartar emetic). Boiling solutions of alkaline hydroxids convert it into antimonic acid.

**Antimony Pentoxid**—*Antimonic anhydrid*—$Sb_2O_5$—320—is obtained by heating metantimonic acid to dull redness. It is an amorphous, tasteless, odorless, pale lemon-yellow colored solid; very sparingly soluble in water and in acids. At a red heat it is decomposed into $Sb_2O_4$ and O.

**Antimony Antimonate**—*Intermediate oxid*—*Diantimonic tetroxid*—$Sb_2O_4$—304—occurs in nature and is formed when the oxids or hydrates of Sb are strongly heated, or when the lower stages of oxidation or the sulfids are oxidized by $HNO_3$, or by fusion with sodium nitrate. It is soluble in $H_2O$; but is decomposed by HCl, hydropotassic tartrate, and potash.

**Antimony Acids.**—The normal antimonous acid, $H_3SbO_3$, corresponding to $H_3PO_3$, is unknown; but the series of antimonic acids: ortho, $H_3SbO_4$; pyro, $H_4Sb_2O_7$; and meta, $HSbO_3$, is complete, either in the form of salts, or in that of the free acids. There also exists, in its sodium salt, a derivative of the lacking antimonous acid: **metantimonous acid**, $HSbO_2$.

The compound sometimes used in medicine under the name *washed diaphoretic antimony* is potassium metantimonate, united with an excess of the pentoxid: $2KSbO_3$, $Sb_2O_5$. The hydropotassic pyroantimonate, $K_2H_2Sb_2O_7 6Aq$ is a valuable reagent for the sodium compounds. It is obtained by calcining a mixture of one part of antimony with four parts potassium nitrate, and fusing the product with its own weight of potassium carbonate.

**Sulfids of Antimony.**—**Antimony Trisulfid**—*Sesquisulfid of antimony*—*Black antimony*—**Antimonii sulfidum** (U. S.)—**Antimonium nigrum** (Br.)—$Sb_2S_3$—336—is the chief ore of antimony; and is formed when $H_2S$ is passed through a solution of tartar emetic.

The native sulfid is a steel-gray, crystalline solid; the artificial product, an orange-red, or brownish red, amorphous powder. The **crude antimony** of commerce is in conical loaves, prepared by simple fusion of the native sulfid. It is soft, fusible, readily pulverized, and has a bright metallic luster.

Heated in air, it is decomposed into $SO_2$ and a brown, vitreous, more or less transparent mass, composed of varying proportions of oxid and oxysulfids, known as **crocus**, or **liver**, or **glass of antimony**. $Sb_2S_3$ is an anhyrid, corresponding to which are salts known as **thioantimonites**, having the general formula $M'_2HSbS_3$. If an excess of $Sb_2S_3$ be boiled with a solution of potash or soda, a liquid is obtained, which contains an alkaline thioantimonite, and an excess of $Sb_2S_3$. If this solution be filtered, and decomposed by an acid while still hot, an orange-colored, amorphous precipitate is produced, which is the **antimonium sulfuratum** (U. S.; Br.), and consists of a mixture, in varying proportions, of $Sb_2S_3$ and $Sb_2O_3$. If, however, the solution be allowed to cool, a brown, voluminous, amorphous precipitate separates, which consists of antimony trisulfid and trioxid, potassium or sodium sulfid, and alkaline thioantimonite in varying proportions; and is known as **Kermes mineral**. If now the solution from which the Kermes has been separated, be decomposed with $H_2SO_4$ a reddish

yellow substance separates, which is the **golden sulfuret of antimony**, and consists of a mixture of $Sb_2S_3$ and $Sb_2S_5$. The precipitate obtained when $H_2S$ acts upon a solution of an antimonial compound is, according to circumstances, $Sb_2S_3$ or $Sb_2S_5$, mixed with free S. By the action of HCl on $Sb_2S_3$, $H_2S$ is produced.

**Antimony Pentasulfid**—$Sb_2S_5$—400—is obtained by decomposing an alkaline thioantimonate by an acid. It is a dark orange-red, amorphous powder, readily soluble in solutions of the alkalies, and alkaline sulfids, with which it forms **thioantimonates.**

An oxysulfid, $Sb_6S_6O_3$, is obtained by the action of a solution of sodium thiosulfate upon $SbCl_3$ or tartar emetic. It is a fine red powder, used as a pigment, and called **antimony cinnabar or antimony vermilion.**

**Action of Antimony Compounds on the Economy.** — The compounds of antimony are poisonous, and act with greater or less energy as they are more or less soluble. The compound which is most frequently the cause of antimonial poisoning is tartar emetic (q. v.), which has caused death in a quantity of three grains, in divided doses, although recovery has followed the ingestion of half an ounce in several instances. Indeed, the chances of recovery seem to be better with large, than with small doses, probably owing to the more rapid and complete removal of the poison by vomiting with large doses. Antimonials have been sometimes criminally administered in small and repeated doses, the victim dying of exhaustion. In such a case an examination of the urine will reveal the cause of the trouble.

If vomiting have not occurred in cases of acute antimonial poisoning it should be provoked by warm water, or the stomach should be washed out. Tannin in some form (decoction of oak bark, cinchona, nutgalls, tea) should then be given, with a view to rendering any remaining poison insoluble.

Medicinal antimonials are very liable to contamination with arsenic.

**Analytical Characters of Antimonial Compounds.**—(1) With $H_2S$ in acid solution: an orange-red ppt., soluble in $NH_4HS$ and in hot HCl.

(2) A strip of bright copper, suspended in a boiling solution of an Sb compound, acidulated with HCl, is coated with a blue-gray deposit. This deposit when dried (on the copper), and heated in a tube, open at both ends yields a white, *amorphous* sublimate (see No. 5, p. 131).

(3) Antimonial compounds yield a deposit by Marsh's test, similar to that obtained with arsenical compounds, but differing in the particulars given above (see No. 6, p. 134).

# IV. BORON GROUP.

## BORON.

*Symbol*=B—*Atomic weight*=11 (O=16:11; H=1:10.91)—*Molecular weight*=22 (?)=*Isolated by Davy in* 1807.

Boron occurs in nature in the borates of Ca, Mg, and Na, principally as sodium pyroborate (borax). It constitutes a group by itself; it is trivalent in all of its compounds; it forms but one oxid, which is the anhydrid of a tribasic acid; and it forms no compound with H.

It is separable in two allotropic modifications. **Amorphous boron** is prepared by decomposition of the oxid, by heating with metallic potassium or sodium. It is a greenish brown powder; sparingly soluble in $H_2O$; infusible; and capable of direct union with Cl, Br, O, S, and N. **Crystallized boron** is produced when the oxid, chlorid or fluorid is reduced by Al. It crystallizes in quadratic prisms; more or less transparent, and varying in color from a faint yellow to deep garnet-red; very hard; sp. gr. 2.68. It burns when strongly heated in O, and readily in Cl; it also combines with N, which it is capable of removing from $NH_3$ at a high temperature.

**Boron Trioxid.**—*Boric* or *boracic anhydrid*—$B_2O_3$—70—is obtained by heating boric acid to redness in a platinum vessel. It is a transparent, glass-like mass, used in blowpipe analysis under the name **vitreous boric acid.**

**Boric Acids.**—**Boric Acid**—*Boracic acid*—*Orthoboric acid*—**Acidum boricum** (U. S.)—$H_3BO_3$—62—occurs in nature; and is prepared by slowly decomposing a boiling, concentrated solution of borax, with an excess of $H_2SO_4$, and allowing the acid to crystallize.

It forms brilliant, crystalline plates, unctuous to the touch; odorless; slightly bitter; soluble in 34 parts $H_2O$ at 10° (50° F.); soluble in alcohol. Its solution reddens litmus, but turns turmeric paper brown. When its aqueous solution is distilled, a portion of the acid passes over.

Boric acid readily forms esters with the alcohols. When heated with ethylic alcohol, **ethyl borate** is formed, which burns with a green flame. Heated with glycerol, a soluble, neutral ester is formed, known as **boroglycerid**, and used as an antiseptic.

If $H_3BO_3$ be heated for some time at 80° (176° F.), it loses $H_2O$ and is converted into **metaboric acid**, $HBO_2$. If maintained at 100° (212° F.) for several days, it loses a further quantity of $H_2O$, and is converted into **tetraboric** or **pyroboric acid**, $H_2B_4O_7$, whose sodium salt is borax.

# V. CARBON GROUP.

## CARBON — SILICON.

The elements of this group are bivalent or quadrivalent. The saturated oxid of each is the anhydrid of a dibasic acid. They are both combustible, and each occurs in three allotropic forms.

## CARBON.

*Symbol*=C—*Atomic weight*=12 (O=16:12; H=1:11.9)—*Molecular weight*=24 (?).

**Occurrence.**—Free in its three allotropic forms: The **diamond** in octahedral crystals; in alluvial sand, clay, sandstone, and conglomerate; **graphite**, in amorphous or imperfectly crystalline forms; **amorphous**, in the different varieties of anthracite and bituminous coal, jet, etc. In combination, it is very widely distributed in the so-called organic substances.

**Properties.—Diamond.**—The crystals of diamond, which is almost pure carbon, are usually colorless or yellowish, but may be blue, green, pink, brown or black. It is the hardest substance known, and the one which refracts light the most strongly. Its index of refraction is 2.47 to 2.75. It is brittle; a bad conductor of heat and of electricity; sp. gr. 3.50 to 3.55. When very strongly heated in air it burns, without blackening, to carbon dioxid.

**Graphite** is a form of carbon almost as pure as the diamond, capable of crystallizing in hexagonal plates; sp. gr. 2.2; dark gray in color; opaque; soft enough to be scratched by the nail; and a good conductor of electricity. It is also known as **black lead** or **plumbago.** It has been obtained artificially, by allowing molten cast-iron, containing an excess of carbon, to cool slowly, and dissolving the iron in HCl. When oxidized with potassium chlorate and nitric acid it yields **graphitic acid,** $C_{11}H_4O_5$.

**Amorphous carbon** is met with in a great variety of forms, natural and artificial, in all of which it is black; sp. gr. 1.6–2.0; more or less porous; and a conductor of electricity.

**Anthracite** coal is hard and dense; it does not flame when burning; is difficult to kindle, but gives great heat with a suitable draught. It contains 80–90 per cent. of carbon. **Bituminous** coal differs from anthracite in that, when burning, it gives off gases, which produce a flame. Some varieties are quite soft, while others, such as jet, are hard enough to assume a high polish. It is usually compact in texture, and very frequently contains impressions of

leaves, and other parts of plants. It contains about 75 per cent. of carbon.

**Charcoal, carbo ligni,** U. S., is obtained by burning woody fiber, with an insufficient supply of air. It is brittle and sonorous; has the form of the wood from which it was obtained, and retains all the mineral matter present in the woody tissue. Its sp. gr. is about 1.57. It has the power of condensing within its pores odorous substances and large quantities of gases; 90 volumes of ammonia, 55 of hydrogen sulfid, 9.25 of oxygen. This property is taken advantage of in a variety of ways. Its power of absorbing odorous bodies renders it valuable as a disinfecting and filtering agent, and in the prevention of putrefaction and fermentation of certain liquids. The efficacy of charcoal as a filtering material is due also, in a great measure, to the oxidizing action of the oxygen condensed in its pores; indeed, if charcoal be boiled with dilute HCl, dried, and heated to redness, the oxidizing action of the oxygen, which it thus condenses, is very energetic.

When small strips of wood are heated to redness in a current of vapor of carbon disulfid, or of hydrocarbons, **metallic carbon** is produced. This is very sonorous, and is a very good conductor of heat and of electricity. The filaments in incandescent electric lamps are prepared from vegetable parchment or bamboo fiber in a similar manner.

**Lamp-black** is obtained by incomplete combustion of some resinous or tarry substance, or natural gas, the smoke or soot from which is directed into suitable condensing chambers. It is a light, amorphous powder, and contains a notable quantity of oily and tarry material, from which it may be freed by heating in a covered vessel. It is used in the manufacture of printer's ink.

**Coke** is the substance remaining in gas retorts, after the distillation of bituminous coal, in the manufacture of illuminating gas. It is a hard, grayish substance, usually very porous, dense, and sonorous. When iron retorts are used, a portion of the gaseous products are decomposed by contact with the hot iron surface, upon which there is then deposited a layer of very hard, compact, grayish carbon, which is a good conductor of electricity.

**Animal charcoal** is obtained by calcining animal matters in closed vessels. If prepared from bones it is known as **bone-black, carbo animalis,** U. S.; if from ivory, **ivory black.** The latter is used as a pigment, the former as a decolorizing agent. Bones yield about 60 per cent. of bone-black, which contains, besides carbon, nitrogen and the phosphates and other mineral substances of the bones. It possesses in a remarkable degree the power of absorbing coloring matters. When its decolorizing power is lost by saturation with pig-

mentary bodies, it may be restored, although not completely, by calcination. For certain purposes purified animal charcoal, i. e., freed from mineral matter, **carbo animalis purificatus**, U. S., is required, and is obtained by extracting the commercial article with HCl, and washing it thoroughly. Its decolorizing power is diminished by this treatment. Animal charcoal has the power of removing from a solution certain crystalline substances, notably the alkaloids, and a method has been suggested for separating these bodies from organic mixtures by its use.

All forms of carbon are insoluble in any known liquid.

*Chemical.*—All forms of C combine with O at high temperatures, with light and heat. The product of the union is carbon dioxid if the supply of air or O be sufficient; but if O be present in limited quantity, carbon monoxid is formed. The affinity of C for O renders it a valuable reducing agent. Many metallic oxids are reduced, when heated with C, and steam is decomposed when passed over red-hot C: $H_2O+C=CO+H_2$. At elevated temperatures C also combines directly with S, to form carbon disulfid. With H, carbon also combines directly, under the influence of the voltaic arc.

For Compounds of Carbon, see page 216.

## SILICON.

*Symbol*=Si—*Atomic weight*=28 (O=16:28.4; H=1:28.17)—*Molecular weight*=56 (?)—*Discovered by Davy*, 1807—*Name from* silex=*flint.*

Also known as **silicium**; occurs in three allotropic forms: **Amorphous silicon**, formed when silicon chlorid is passed over heated K or Na, is a dark brown powder, heavier than water. When heated in air, it burns with a bright flame to the dioxid. It dissolves in potash and in hydrofluoric acid, but is not attacked by other acids. **Graphitoid silicon** is obtained by fusing potassium fluosilicate with aluminium. It forms hexagonal plates, of sp. gr. 2.49, which do not burn when heated to whiteness in O, but may be oxidized at that temperature, by a mixture of potassium chlorate and nitrate. It dissolves slowly in alkaline solutions, but not in acids. **Crystallized silicon**, corresponding to the diamond, forms crystalline needles, which are only attacked by a mixture of nitric and hydrofluoric acids.

Silicon, although closely related to C, exists in nature in comparatively few compounds. It has been caused to form artificial combinations, however, which indicate its possible capacity to exist in substances corresponding to those C compounds commonly known as

organic, e. g., **silicichloroform** and **silicibromoform**, $SiHCl_3$ and $SiHBr_3$.

**Hydrogen Silicid**—$SiH_4$—32—is obtained as a colorless, insoluble, spontaneously inflammable gas, by passing the current of a galvanic battery of twelve cells through a solution of common salt, using a plate of aluminium, alloyed with silicon, as the positive electrode.

**Silicon Chlorid**—$SiCl_4$—170—a colorless, volatile liquid, having an irritating odor; sp. gr. 1.52; boils at 59° (138.2° F.); formed when Si is heated to redness in Cl.

**Silicic Oxid**—*Silicic anhydrid*—*Silex*—$SiO_2$—60—is the most important of the compounds of silicon. It exists in nature in the different varieties of quartz, and in the rocks and sands containing that mineral, in agate, carnelian, flint, etc. Its purest native form is **rock crystal.** Its hydrates occur in the opal, and in solution in natural waters. When crystallized, it is fusible with difficulty. When heated to redness with the alkaline carbonates, it forms **silicates,** which solidify to glass-like masses, on cooling. It unites with $H_2O$ to form a number of acid hydrates. The normal hydrate, $H_4SiO_4$, has not been isolated, although it probably exists in the solution obtained by adding an excess of HCl to a solution of sodium silicate. A gelatinous hydrate, soluble in water and in acids and alkalies, is obtained by adding a small quantity of HCl to a concentrated solution of sodium silicate.

**Hydrofluosilicic Acid**—$H_2SiF_6$—144—is obtained in solution by passing the gas disengaged by gently heating a mixture of equal parts of fluorspar and pounded glass and 6 pts. $H_2SO_4$ through water; the disengagement tube being protected from moisture by a layer of mercury. It is used in analysis as a test for K and Na.

**Silicon Carbide**—SiC—is produced by the action of a powerful electric current upon a mixture of coke and aluminium silicate. It forms blue crystals, is very hard, and is used as a polishing agent under the name **Carborundum.**

## VI. VANADIUM GROUP.

### VANADIUM—NIOBIUM—TANTALUM.

The elements of this group resemble those of the N group, but are usually quadrivalent.

**Vanadium**—V—51.2—a brilliant, crystalline metal; sp. gr.=5.5; which forms a series of oxids similar to those of N. No salts of V are known, but salts of vanadyl (VO) are numerous, and are used in the manufacture of anilin **black.**

**Niobium (Columbium)**—Nb—94—a bright, steel-gray metal; sp. gr. 7.06; which burns in air to $Nb_2O_5$ and in Cl to $NbCl_5$; not attacked by acids.

**Tantalum**—Ta—183—closely resembles Nb in its chemical characters.

## VII. MOLYBDENUM GROUP.

MOLYBDENUM—TUNGSTEN—OSMIUM.

The position of this group is doubtful; and it is probable that the lower oxids will be found to be basic in character, in which case the group should be transferred to the third class.

**Molybdenum**—Mo—96—a brittle white metal. The oxid $MoO_3$, *molybdic anhydrid*, combines with $H_2O$ to form a number of acids; the ammonium salt of one of which is used as a reagent for $H_3PO_4$; with which it forms a conjugate acid, *phosphomolybdic acid*, used as a reagent for the alkaloids.

**Tungsten**—*Wolfram*—W—184—a hard, brittle metal; sp. gr. 17.4. The oxid, $WO_3$, *tungstic anhydrid*, is a yellow powder, forming with $H_2O$ several acid hydrates; one of which, *metatungstic acid*, is used as a test for the alkaloids, as are also the conjugate *silicotungstic* and *phosphotungstic acids*. Tissues impregnated with *sodium tungstate* are rendered uninflammable.

**Osmium**—Os—191—occurs in combination with Ir in Pt ores; combustible and readily oxidized to $OsO_4$. This oxid, known as *osmic acid*, forms colorless crystals, soluble in $H_2O$, which give off intensely irritating vapors. It is used as a staining agent by histologists, and also in dental practice.

## CLASS III.—AMPHOTERIC ELEMENTS.

**Elements whose Oxids unite with Water, some to form Bases, others to form Acids; which form Oxysalts.**

# I. GOLD GROUP.

### GOLD.

*Symbol* = Au (*Aurum*) — *Atomic weight* = 197 (O = 16 : 197.2; H=1 : 195.63)—*Molecular weight*=394 (?)—*Sp. gr.*=19.258–19.367 —*Fuses at* 1200° (2192° F.).

This, the only member of the group, forms two series of compounds; in one, AuCl, it is univalent; in the other, $AuCl_3$, trivalent. Its hydroxid, auric acid, $Au(OH)_3$, corresponds to the oxid, $Au_2O_3$. Its oxysalts are unstable.

It is yellow or red by reflected light, green by transmitted light, reddish-purple when finely divided; not very tenacious; softer than silver; very malleable and ductile. It is not acted on by $H_2O$ or air, at any temperature, nor by any single acid. It combines directly with Cl, Br, I, P, Sb, As and Hg. It dissolves in nitromuriatic acid as auric chlorid. It is oxidized by alkalies in fusion on contact with air. Gold coin and jewelry always contain silver or copper, or both. The proportion of gold present is expressed in 1000ths in coin, and in "carats" in jewelry; pure gold being 24 carats fine.

**Aurous Chlorid**—AuCl—is produced when auric chlorid is heated to 185° (365° F.).

**Auric Chlorid**—*Gold trichlorid*—$AuCl_3$—303.6—obtained by dissolving Au in aqua regia, evaporating at 100° (212° F.), and purifying by crystallization from $H_2O$. Deliquescent, yellow prisms, very soluble in $H_2O$, alcohol and ether; readily decomposed, with separation of Au, by contact with P, or with reducing agents. Its solution, treated with the chlorids of tin, deposits a purple double stannate of Sn and Au, called "*purple of Cassius.*" With alkaline chlorids it forms double chlorids, **chloraurates (auri et sodii chloridum, U. S.)**.

**Aurous Oxid**—$Au_2O_3$—is a violet powder, formed by the action of KHO on AuCl. **Auric Oxid**, $Au_2O_3$, is brown, and very unstable.

**Analytical Characters.**—(1) With $H_2S$, from neutral or acid solution: a blackish-brown ppt. in the cold; insoluble in $HNO_3$ and HCl; soluble in aqua regia, and in yellow $NH_4HS$. (2) With stannous chlorid and a little chlorin water, a purple-red ppt., insoluble in HCl. (3) With ferrous sulfate: a brown deposit, which assumes the luster of gold when dried and burnished.

## II. IRON GROUP.

### CHROMIUM—MANGANESE—IRON.

The elements of the group form two series of compounds. In one they are bivalent, as in $Fe''Cl_2$ or $Mn''SO_4$, while in the other they are quadrivalent; but when quadrivalent, the atoms do not enter into combination singly, but grouped, two together, to form a hexavalent unit $\left[\begin{matrix}Fe\equiv\\ |\\ Fe\equiv\end{matrix}\right]^{vi}$, as in $(Fe_2)^{vi}Cl_6$, $(Cr_2)^{vi}O_3$. They form several oxids; of which the oxid $MO_3$ is an anhydrid, corresponding to which are acids and salts. Most of the other oxids are basic.

### CHROMIUM.

*Symbol* = Cr — *Atomic weight* = 52 (O=16:52.1; H=1:51.69)— *Molecular weight*=104.12 (?)—*Sp. gr.*=6.8—*Discovered by Vauquelin*, 1797—*Name from* χρῶμα = color.

Occurs in nature principally as chrome ironstone, a double oxid of Cr and Fe. The element is separated with difficulty by reduction of its oxid by charcoal, or of its chlorid by sodium. It is a hard, crystalline, almost infusible metal. Combines with O only at a red heat. It is not attacked by acids, except HCl; is readily attacked by alkalies.

**Chromic Oxid**—*Sesquioxid, or green oxid of chromium*—$Cr_2O_3$—152.2—obtained, amorphous, by calcining a mixture of potassium dichromate and starch, or, crystallized, by heating neutral potassium chromate to redness in Cl.

It is green; insoluble in $H_2O$, acids and alkalies; fusible with difficulty, and not decomposed by heat; not reduced by H. At a red heat in air, it combines with alkaline hydroxids and nitrates, to form chromates. It forms two series of salts, the terms of one of which are green, those of the other violet. The alkaline hydroxids separate a bluish-green hydrate from solutions of the green salts, and a bluish violet hydrate from those of the violet salts.

**Chromium green, or emerald green,** is a green hydrate, formed by decomposing a double borate of chromium and potassium by $H_2O$. It is used in the arts as a substitute for the arsenical greens, and is non-poisonous.

**Chromic Anhydrid—Acidum chromicum** (U. S.)—$CrO_3$—100—is formed by decomposing a solution of potassium dichromate by excess of $H_2SO_4$, and crystallizing.

It crystallizes in deliquescent, crimson prisms, very soluble in $H_2O$ and in dilute alcohol. It is a powerful oxidant, capable of igniting strong alcohol.

The true chromic acid has not been isolated, but salts are known which correspond to three acid hydrates: $H_2CrO_4$ = chromic acid; $H_2Cr_2O_7$ = dichromic acid; and $H_2Cr_3O_{10}$ = trichromic acid.

**Chlorids.**—Two chlorids and one oxychlorid of chromium are known. **Chromous chlorid,** $CrCl_2$, is a white solid, soluble, with a blue color, in $H_2O$. **Chromic chlorid,** $(Cr_2)Cl_6$, forms large red crystals, insoluble in $H_2O$ when pure.

**Sulfates.**—A *violet* sulfate crystallizes in octahedra, $(Cr)_2(SO_4)_3$+ 15 Aq, and is very soluble in $H_2O$. At 100° it is converted into a *green* salt, $(Cr)_2(SO_4)_3$+5 Aq, soluble in alcohol; which, at higher temperatures, is converted into the red, insoluble, anhydrous salt. Chromic sulfate forms double sulfates, containing 24 Aq, with the alkaline sulfates. (See Alums.)

**Analytical Characters.**—CHROMOUS SALTS.—(1) Potash: a brown ppt. (2) Ammonium hydroxid: greenish white ppt. (3) Alkaline sulfids: black ppt. (4) Sodium phosphate: blue ppt.

CHROMIC SALTS.—(1) Potash: green ppt.; an excess of precipitant forms a green solution, from which $Cr_2O_3$ separates on boiling. (2) Ammonium hydroxid: greenish-gray ppt. (3) Ammonium sulfhydrate: greenish ppt.

CHROMATES.—(1) $H_2S$ in acid solution: brownish color, changing to green. (2) Ammonium sulfhydrate: greenish ppt. (3) Barium chlorid: yellowish ppt. (4) Silver nitrate: brownish red ppt., soluble in $HNO_3$ or $NH_4HO$. (5) Lead acetate: yellow ppt., soluble in potash, insoluble in acetic acid.

**Action on the Economy.**—*Chromic anhydrid* oxidizes organic substances, and is used as a caustic.

The *chromates*, especially potassium dichromate (*q. v.*), are irritants, and have a distinctly poisonous action as well. Workmen handling the dichromate are liable to a form of chronic poisoning.

In acute chromium poisoning, emetics, and subsequently magnesium carbonate in milk, are to be given.

## MANGANESE.

*Symbol*=Mn—*Atomic weight*=55 (O=16:55; H=1:54.56)—*Molecular weight*=110 (?)—*Sp. gr.*=7.138–7.206.

Occurs chiefly in pyrolusite, $MnO_2$, hausmanite, $Mn_3O_4$, braunite, $Mn_2O_3$, and manganite, $Mn_2O_3$, $H_2O$. A hard, grayish, brittle metal; fusible with difficulty; obtained by reduction of its oxids by C at a

white heat. It is not readily oxidized by cold, dry air; but is superficially oxidized when heated. It decomposes $H_2O$, liberating H, and dissolves in dilute acids.

**Oxids.**—Manganese forms six oxids, or compounds representing them: **Manganous oxid,** MnO; **manganoso-manganic oxid,** $Mn_3O_4$; **manganic oxid,** $Mn_2O_3$; **permanganic oxid,** $MnO_2$, and **permanganic anhydrid,** $Mn_2O_7$, are known free. **Manganic anhydrid,** $MnO_3$, has not been isolated. MnO and $Mn_2O_3$ are basic; $Mn_3O_4$ and $MnO_2$ are indifferent oxids; and $MnO_3$ and $Mn_2O_7$ are anhydrids, corresponding to the **manganates** and **permanganates.**

**Permanganic oxid**—*Manganese dioxid, or black oxid*—**Mangani oxidum nigrum** (U. S.); **Manganesii ox. nig.** (Br.)—$MnO_2$—86—exists in nature as **pyrolusite,** the principal ore of manganese, in steel gray, or brownish black, imperfectly crystalline masses.

At a red heat it loses 12 per cent. of O: $3MnO_2=Mn_3O_4+O_2$; and at a white heat, a further quantity of O is given off: $2Mn_3O_4=6MnO+O_2$. Heated with $H_2SO_4$, it gives off O, and forms manganous sulfate: $2MnO_2+2H_2SO_4=2MnSO_4+2H_2O+O_2$. With HCl it yields manganous chlorid, $H_2O$ and Cl: $MnO_2+4HCl=MnCl_2+2H_2O+Cl_2$. It is not acted on by $HNO_3$.

**Chlorids.**—Two chlorids of Mn are known: **manganous chlorid,** $MnCl_2$, a pink, deliquescent, soluble salt, occurring, mixed with ferric chlorid, in the waste liquid of the preparation of Cl; and **manganic chlorid,** $Mn_2Cl_6$.

**Salts of Manganese.**—Manganese forms two series of salts: **Manganous salts,** containing $Mn''$; and **manganic salts,** containing $(Mn_2)^{vi}$; the former are colorless or pink, and soluble in water; the latter are unstable.

**Manganous Sulfate—Mangani sulfas** (U. S.)—$MnSO_4+n$Aq—$150+n18$—is formed by the action of $H_2SO_4$ on $MnO_2$. Below 6° (42.8° F.) it crystallizes with 7 Aq, and is isomorphous with ferrous sulfate; between 7°–20° (44.6°–68° F.) it forms crystals with 5 Aq, and is isomorphous with cupric sulfate; between 20°–30° (68°–86° F.) it crystallizes with 4 Aq. It is rose-colored, darker as the proportion of Aq increases, soluble in $H_2O$, insoluble in alcohol. With the alkaline sulfates it forms double salts, with 6 Aq.

**Analytical Characters.**—MANGANOUS.—(1) Potash: white ppt., turning brown. (2) Alkaline carbonates: white ppts. (3) Ammonium sulfhydrate: flesh-colored ppt., soluble in acids, sparingly soluble in excess of precipitant. (4) Potassium ferrocyanid: faintly reddish white ppt., in neutral solution; soluble in HCl. (5) Potassium cyanid: rose-colored ppt. forming brown solution with excess.

MANGANIC.—(1) $H_2S$: ppt. of sulfur. (2) Ammonium sulfhydrate: flesh-colored ppt. (3) Potassium ferrocyanid: greenish ppt. (4) Po-

tassium ferricyanid: brown ppt. (5) Potassium cyanid: light brown ppt.

MANGANATES—are green salts, whose solutions are only stable in presence of excess of alkali, and turn brown when diluted and acidulated.

PERMANGANATES—form red solutions, which are decolorized by $SO_2$, other reducing agents, and many organic substances.

## IRON.

*Symbol* = Fe (*Ferrum*) — *Atomic weight*=56 (O = 16:56; H= 1:55.56)—*Molecular weight*=111.8 (?)—*Sp. gr.*=7.25–7.9—*Fuses at* 1600° (2912° F.)—*Name from the Saxon*, iren.

**Occurrence.**—Free, in small quantity only, in platinum ores and meteorites. As $Fe_2O_3$ in *red hæmatite* and *specular iron;* as hydrates of $Fe_2O_3$ in *brown hæmatite* and *oölitic iron;* as $Fe_3O_4$ in *magnetic iron;* as $FeCO_3$ in *spathic iron*, *clay ironstone* and *bog ore;* and as $FeS_2$ in *pyrites*. It is also a constituent of most soils and clays, exists in many mineral waters, and in the red blood pigment of animals.

**Preparation.**—In working the ores, reduction is first effected in a *blast furnace*, into which alternate layers of ore, coal and limestone are fed from the top, while air is forced in from below. In the lower part of the furnace $CO_2$ is produced, at the expense of the coal; higher up it is reduced by the incandescent fuel to CO, which, at a still higher point, reduces the ore. The fused metal, so liberated, collects at the lowest point, under a layer of *slag;* and is drawn off to be cast as *pig iron*. This product is then purified, by burning out impurities, in the process known as *puddling*.

*Pure iron* is prepared by reduction of ferrous chlorid, or of ferric oxid, by H at a temperature approaching redness.

**Varieties.**—*Cast iron* is a brittle, white or gray, crystalline metal, consisting of Fe 89–90%; C 1–4.5%; and Si, P, S, and Mn. As *pig iron*, it is the product of the blast-furnace.

*Wrought*, or *bar iron*, is a fibrous, tough metal, freed in part from the impurities of cast iron, by *refining* and *puddling*.

*Steel* is Fe combined with a quantity of C, less than that existing in cast iron, and greater than that in bar iron. It is prepared by *cementation;* which consists in causing bar iron to combine with C; or by the *Bessemer method;* which, as now used, consists in burning the C out of molten cast iron, to which the proper proportion of C is then added in the shape of *spiegel eisen*, an iron rich in Mn and C.

The purest forms of commercial iron are those used in piano-

strings, the teeth of carding machines and electro magnets; known as *soft iron.*

*Reduced iron*—**Ferrum reductum** (U. S.)—**Fer. redactum** (Br.)—is Fe, more or less mixed with $Fe_2O_3$ and $Fe_3O_4$, obtained by heating $Fe_2O_3$ in H.

**Properties.**—*Physical.*—Pure iron is silver white, quite soft; crystallizes in cubes or octahedra. *Wrought iron* is gray, hard, very tenacious, fibrous, quite malleable and ductile, capable of being welded, highly magnetic, but only temporarily so. *Steel* is gray, very hard and brittle if *tempered*, soft and tenacious if not, permanently magnetic.

*Chemical.*—Iron is not altered by dry air at the ordinary temperature. At a red heat it is oxidized. In damp air it is converted into a hydrate, *iron rust*. *Tinplate* is sheet iron, coated with tin; *galvanized iron* is coated with zinc, to preserve it from the action of damp air.

Iron unites directly with Cl, Br, I, S, N, P, As, and Sb. It dissolves in HCl as ferrous chlorid, while H is liberated. Heated with strong $H_2SO_4$, it gives off $SO_2$; with dilute $H_2SO_4$, H is given off and ferrous sulfate formed. Dilute $HNO_3$ dissolves Fe, but the concentrated acid renders it *passive*, when it is not dissolved by either concentrated or dilute $HNO_3$, until the passive condition is destroyed by contact with Pt, Ag or Cu, or by heating to 40° (104° F.).

**Compounds of Iron.—Oxids.**—Three oxids of iron exist free: FeO; $Fe_2O_3$; $Fe_3O_4$.

**Ferrous Oxid.**—*Protoxid of iron*—FeO—72—is formed by heating $Fe_2O_3$ in CO or $CO_2$.

**Ferric Oxid.**—*Sesquioxid or peroxid of iron—Colcothar—Jeweler's rouge—Venetian red*—$Fe_2O_3$—160—occurs in nature (see above), and is formed when ferrous sulfate is strongly heated, as in the manufacture of pyrosulfuric acid. It is a reddish, amorphous solid, is a weak base, and is decomposed at a white heat into O and $Fe_3O_4$.

**Magnetic Oxid**—*Black oxid—Ferri oxidum magneticum* (Br.)—$Fe_3O_4$—232—is the **natural loadstone**, and is formed by the action of air, or steam, upon iron at high temperatures. It is probably a compound of ferrous and ferric oxids (FeO, $Fe_2O_3$), as acids produce with it mixtures of ferrous and ferric salts.

**Hydrates.—Ferrous.**—When a solution of a ferrous salt is decomposed by an alkaline hydroxid, a greenish-white hydroxid, $FeH_2O_2$, is deposited; which rapidly absorbs O from the air, with formation of ferric hydroxid.

**Ferric.**—When an alkali is added to a solution of a ferric salt, a brown, gelatinous precipitate is formed, which is the **normal ferric hydroxid** $(Fe)_2H_6O_6$ = **Ferri peroxidum hydratum** (U. S.); Fer.

**perox. humidum** (Br.). It is not formed in the presence of fixed organic acids, or of sugar in sufficient quantity. If preserved under $H_2O$, it is partly oxidized, forming an oxyhydrate which is incapable of forming ferrous arsenate with $As_2O_3$.

If the hydroxid $(Fe_2)H_6O_6$, be dried at 100° (212° F.), it loses $2H_2O$, and is converted into $(Fe_2)O_2$, $H_2O_2$, which is the *Ferri peroxidum hydratum* (Br.).

If the normal hydroxid be dried *in vacuo*, it is converted into $(Fe_2)_2H_6O_9$, and this, when boiled for some hours with $H_2O$, is converted into the **colloid** or **modified hydrate** $(Fe_2)H_2O_4$ (†), which is brick-red in color, almost insoluble in $HNO_3$ and HCl, gives no Prussian blue reaction, and forms a turbid solution with acetic acid. If recently precipitated ferric hydroxid be dissolved in solution of ferric chlorid or acetate, and subjected to dialysis, almost all the acid passes out, leaving in the dialyzer a dark red solution, which probably contains this colloid hydrate, and which is instantly coagulated by a trace of $H_2SO_4$, by alkalies, many salts, and by heat; **dialyzed iron.**

**Ferric Acid.**—$H_2FeO_4$.—Neither the free acid nor the oxid, $FeO_3$, is known in the free state; the **ferrates**, however, of Na, K, Ba, Sr, and Ca are known.

**Sulfids.**—**Ferrous Sulfid**—*Protosulfid of iron*—FeS—88—is formed:

(1) By heating a mixture of finely-divided Fe and S to redness; (2) by pressing roll-sulfur on white-hot iron; (3) in a hydrated condition, FeS, $H_2O$, by treating a solution of a ferrous salt with an alkaline sulfhydrate.

The dry sulfid is a brownish, brittle, magnetic solid, insoluble in $H_2O$, soluble in acids with evolution of $H_2S$. The hydrate is a black powder, which absorbs O from the air, turning yellow, by formation of $Fe_2O_3$, and liberation of S. It occurs in the fæces of persons taking chalybeate waters or preparations of iron.

**Ferric Sulfid**—*Sesquisulfid*—$Fe_2S_3$—208—occurs in nature in *copper pyrites*, and is formed when the disulfid is heated to redness.

**Ferric Disulfid**—$FeS_2$—120—occurs in the *white* and *yellow Martial pyrites*, used in the manufacture of $H_2SO_4$. When heated in air, it is decomposed into $SO_2$ and *magnetic pyrites*: $3FeS_2+2O_2=Fe_3S_4+2SO_2$.

**Chlorids.**—**Ferrous Chlorid**—*Protochlorid*—$FeCl_2$—126.9—is produced: (1) by passing dry HCl over red-hot Fe; (2) by heating ferric chlorid in H; (3) as a hydrate, $FeCl_2$, $4H_2O$, by dissolving Fe in HCl.

The anhydrous compound is a yellow, crystalline, volatile, and very soluble solid. The hydrated is in greenish, oblique rhombic

prisms, deliquescent and very soluble in $H_2O$ and alcohol. When heated in air it is converted into ferric chlorid, and an oxychlorid.

**Ferric Chlorid**—*Sesquichlorid*—*Perchlorid*—**Ferri chloridum** (U. S.)—$Fe_2Cl_6$—324.7—is produced, in the anhydrous form, by heating Fe in Cl. As a hydrate, $Fe_2Cl_6$, $4H_2O$, or $Fe_2Cl_6$, $6H_2O$, it is formed: (1) by solution of the anhydrous compound; (2) by dissolving Fe in aqua regia; (3) by dissolving ferric hydroxid in HCl; (4) by the action of Cl or of $HNO_3$ on solution of ferrous chlorid. It is by the last method that the pharmaceutical product is obtained.

The anhydrous compound forms reddish-violet, crystalline plates, very deliquescent. The hydrates form yellow, nodular, imperfectly crystalline masses, or rhombic plates, very soluble in $H_2O$, soluble in alcohol and ether. In solution, it is converted into $FeCl_2$ by reducing agents. The **Liq. ferri chloridi** (U. S.)=**Liq. fer. perchloridi** (Br.) is an aqueous solution of this compound, containing excess of acid. The **Tinct. fer. chlor.** (U. S.) and **Tinct. fer. perchl.** (Br.) are the solution, diluted with alcohol, and contain ethyl chlorid and ferrous chlorid.

**Bromids.**—**Ferrous Bromid**—$FeBr_2$—215.9—is formed by the action of Br on excess of Fe, in presence of $H_2O$.

**Ferric Bromid**—$Fe_2Br_6$—591.7—is prepared by the action of excess of Br on Fe.

**Iodids.**—**Ferrous Iodid**—**Ferri iodidum** (U. S.; Br.)—$FeI_2$—309.7—is obtained, with $4H_2O$, by the action of I upon excess of Fe in the presence of warm $H_2O$. When anhydrous, it is a white powder; hydrated, it is in green crystals. In air it is rapidly decomposed, more slowly in the presence of sugar.

**Ferric Iodid**—$Fe_2I_6$—873—is formed by the action of excess of I on Fe.

**Salts of Iron.**—**Sulfates.**—**Ferrous Sulfate**—*Protosulfate*—**Green vitriol**—**Copperas**—**Ferri sulfas** (U. S.; Br.)—$FeSO_4+7Aq$—152+126—is formed: (1) by oxidation of the sulfid, $Fe_3S_4$, formed in the manufacture of $H_2SO_4$; (2) by dissolving Fe in dilute $H_2SO_4$.

It forms green, efflorescent, oblique rhombic prisms, quite soluble in $H_2O$, insoluble in alcohol. It loses 6 Aq at 100° (212° F.) (**Ferr. sulf. exsiccatus**, U. S.); and the last Aq at about 300° (572° F.). At a red heat it is decomposed into $Fe_2O_3$; $SO_2$ and $SO_3$. By exposure to air it is gradually converted into a basic ferric sulfate, $(Fe_2)(SO_4)_3$, $5Fe_2O_3$.

**Ferric Sulfates** are quite numerous, and are formed by oxidations of ferrous sulfate under different conditions. The normal sulfate, $(Fe_2)(SO_4)_3$, is formed by treating solution of $FeSO_4$ with $HNO_3$, and evaporating, after addition of one molecule of $H_2SO_4$ for each

two molecules of $FeSO_4$. The **Liq. fer. tersulfatis** (U. S.), contains this salt. It is a yellowish white, amorphous solid.

Of the many basic ferric sulfates, the only one of medical interest is **Monsel's salt**, $5(Fe_2)(SO_4)_3+4Fe_2O_3$, which exists in the **Liq. ferri subsulfatis** (U. S.) and **Liq. fer. persulfatis** (Br.). Its solution is decolorized, and forms a white deposit with excess of $H_2SO_4$.

**Nitrates.—Ferrous Nitrate**—$Fe(NO_3)_2$—179.1—a greenish, unstable salt, formed by double decomposition between barium nitrate and ferrous sulfate; or by the action of $HNO_3$ on FeS.

**Ferric Nitrates.**—The *normal nitrate*—$(Fe_2)(NO_3)_6$—484.2—is obtained in solution by dissolving Fe in $HNO_3$ of sp. gr. 1.115: or by dissolving ferric hydroxid in $HNO_3$. It therefore exists in the *Liq. ferri nitratis* (U. S.). It crystallizes in rhombic prisms with 18 Aq, or in cubes with 12 Aq.

Several basic nitrates are known, all of which are uncrystallizable, and by their presence (as when Fe is dissolved in $HNO_3$ to saturation) prevent the crystallization of the normal salt.

**Phosphates.—Triferrous Phosphate**—$Fe_3(PO_4)_2$—358.—A white precipitate, formed by adding disodic phosphate to a solution of a ferrous salt, in presence of sodium acetate. By exposure to air it turns blue; a part being converted into ferric phosphate. The *ferri phosphas* (Br.) is such a mixture of the two salts. It is insoluble in $H_2O$; sparingly soluble in $H_2O$ containing carbonic or acetic acid.

It is probably this phosphate, capable of turning blue, which sometimes occurs in the lungs in phthisis, in blue pus, and in long-buried bones.

**Ferric Phosphate**—$(Fe_2)(PO_4)_2$—302—is produced by the action of an alkaline phosphate on ferric chlorid. It is soluble in HCl, $HNO_3$, citric and tartaric acids, insoluble in phosphoric acid and in solution of hydrosodic phosphate. The **ferri phosphas** (U. S.) is a compound, or mixture of this salt with disodic citrate, which is soluble in water.

There exist quite a number of basic ferric phosphates.

**Ferric Pyrophosphate**—$(Fe_2)_2(P_2O_7)_3$—746—is precipitated by decomposition of a solution of a ferric compound by sodium pyrophosphate; an excess of the Na salt dissolves the precipitate when warmed, and, on evaporation, leaves the scales of a double salt, $(Fe_2)_2(P_2O_7)_3$, $Na_8(P_2O_7)_2+20$ Aq.

**The ferri pyrophosphas** (U. S.) is a mixture of ferric pyrophosphate, trisodic citrate, and ferric citrate.

**Acetates.—Ferrous Acetate**—$Fe(C_2H_3O_2)_2$—174—is formed by decomposition of ferrous sulfate by calcium acetate, in soluble, silky needles.

**Ferric Acetates.**—The *normal salt* $(Fe_2)(C_2H_3O_2)_6$, is obtained by adding slight excess of ferric sulfate to lead acetate, and decanting after twenty-four hours. It is dark-red, uncrystallizable, very soluble in alcohol, and in $H_2O$. If its solution be heated it darkens suddenly, gives off acetic acid, and contains a basic acetate. When boiled, it loses all its acetic acid, and deposits ferric hydrate. When heated in closed vessels to 100° (212° F.), and treated with a trace of mineral acid, it deposits the modified ferric hydrate.

**Ferrous Carbonate**—$FeCO_3$—*Spathic iron—clay ironstone—bog ore*—116—occurs as an ore of iron, and is obtained, in a hydrated form, by adding an alkaline carbonate to a ferrous salt. It is a greenish, amorphous powder, which on exposure to air turns red by formation of ferric hydrate; a change which is retarded by the presence of sugar, hence the addition of that substance in the **ferri carbonas saccharatus** (U. S.; Br.). It is insoluble in pure $H_2O$, but soluble in $H_2O$ containing carbonic acid, probably as **ferrous bicarbonate**, $H_2Fe(CO_3)_2$, in which form it occurs in chalybeate waters.

**Ferrous Lactate—Ferri Lactas** (U. S.)—$Fe(C_3H_5O_3)_2+3$ Aq—234+54—is formed when iron filings are dissolved in lactic acid. It crystallizes in greenish yellow needles; soluble in $H_2O$; insoluble in alcohol; permanent in air when dry.

**Ferrous Oxalate—Ferri oxalas** (U. S.) $FeC_2O_4+2Aq$—144+36—is a yellow, crystalline powder; sparingly soluble in $H_2O$; formed by dissolving iron filings in solution of oxalic acid.

**Tartrates — Ferrous Tartrate** — $FeC_4H_4O_6+2Aq$ — 204+36. — A white, crystalline powder; formed by dissolving Fe in hot concentrated solution of tartaric acid.

**Ferric Tartrate**—$Fe_2(C_4H_4O_6)_3+3Aq$—556+54.—A dirty yellow, amorphous mass, obtained by dissolving recently precipitated ferric hydroxid in tartaric acid solution, and evaporating below 59° (122° F.).

A number of double tartrates, containing the group $(Fe_2O_2)''$ are also known. Such are: **Ferrico-ammonic tartrate=ferri et ammonii tartras** (U. S.), $(C_4H_4O_6)_2(Fe_2O_2),(NH_4)_2+4Aq$, and **Ferrico-potassic tartrate = ferri et potassii tartras** (U. S.), $(C_4H_4O_6)_2(Fe_2O_2)K_2$. They are prepared by dissolving recently precipitated ferric hydroxid in hot solutions of the hydro-alkaline tartrate. They only react with ferrocyanids and thiocyanates after addition of a mineral acid.

**Citrates.—Ferric Citrate—Ferri citras** (U. S.)—$(Fe_2)(C_6H_5O_7)_2+6Aq$—490+108—is in garnet-colored scales, obtained by dissolving ferric hydrate in solution of citric acid, and evaporating the solution at about 60° (140° F.). It loses 3Aq at 120° (248° F.), and the remainder at 150° (302° F.). If a small quantity of ammonium hydroxid be added, before the evaporation, the product consists of

the modified citrate=ferri et ammonii citras (U. S.), which only reacts with potassium ferrocyanid after addition of HCl.

The various citrates of iron and alkaloids are not definite compounds.

**Ferric Ferrocyanid—Prussian blue**—$(Fe_2)_2(FeC_6N_6)_3+18Aq$—860+324—is a dark-blue precipitate, formed when potassium ferrocyanid is added to a ferric salt. It is insoluble in $H_2O$, alcohol and dilute acids; soluble in oxalic acid solution (blue ink). Alkalies turn it brown.

**Ferrous Ferricyanid—Turnbull's blue**—$Fe_3(Fe_2C_{12}N_{12})+nAq$—592+$n$18—is a dark blue substance produced by the action of potassium ferricyanid on ferrous salts. Heated in air it is converted into Prussian blue and ferric oxid.

**Analytical Characters.**—FERROUS—Are acid; colorless when anhydrous, pale green when hydrated; oxidized by air to basic ferric compounds. (1) Potash: greenish white ppt.; insoluble in excess; changing to green or brown in air. (2) Ammonium hydroxid; greenish ppt.; soluble in excess; not formed in presence of ammoniacal salts. (3) Ammonium sulfhydrate: black ppt.; insoluble in excess; soluble in acids. (4) Potassium ferrocyanid (in absence of ferric salts): white ppt.; turning blue in air. (5) Potassium ferricyanid: blue ppt.; soluble in KHO; insoluble in HCl.

FERRIC—Are acid, and yellow or brown. (1) Potash, or ammonium hydroxid: voluminous, red-brown ppt.; insoluble in excess. (2) Hydrogen sulfid, in acid solution: milky ppt. of sulfur; ferric reduced to ferrous compound. (3) Ammonium sulfhydrate: black ppt.; insoluble in excess; soluble in acids. (4) Potassium ferrocyanid: dark blue ppt.; insoluble in HCl; soluble in KHO. (5) Potassium thiocyanate: dark-red color; prevented by tartaric or citric acid; discharged by mercuric chlorid. (6) Tannin: blue-black color.

## III. URANIUM GROUP.

### URANIUM.

*Symbol*=Ur—*Atomic weight*=239.5 (O=16:239.5; H=1:237.6)—*Sp. gr.*=18.4—*Discovered by Klaproth* (1789).

This element is usually classed with Fe and Cr, or with Ni and Co. It does not, however, form compounds resembling the ferric; it forms a series of well-defined *uranates*, and a series of compounds of the radical *uranyl* $(UO)'$. Standard solutions of its acetate or nitrate are used for the quantitative determination of $H_3PO_4$.

## IV. LEAD GROUP.

### LEAD.

*Symbol* = Pb (*Plumbum*)—*Atomic weight* = 207 (O = 16:206.9; H = 1:205.06)—*Molecular weight* = 414 (?)—*Sp. gr.* = 11.445—*Fuses at* 325° (617° F.)—*Name from* lœd = heavy (*Saxon*).

Lead is usually classed with Cd, Bi, or Cu and Hg. It differs, however, from Bi in being bivalent or quadrivalent, but not trivalent, and in forming no compounds resembling those of bismuthyl (BiO); from Cd, in the nature of its O compounds; and from Cu and Hg in forming no compounds similar to the mercurous and cuprous salts. Indeed, the nature of the Pb compounds is such that the element is best classed in a group by itself, which finds a place in this class by virtue of the existence of potassium plumbate.

**Occurrence.**—Its most abundant ore is **galena**, PbS. It also occurs in **white lead ore**, $PbCO_3$, in **anglesite**, $PbSO_4$, and in **horn lead**, $PbCl_2$.

**Preparation.**—Galena is first roasted with a little lime. The mixture of PbO, PbS, and $PbSO_4$ obtained, is strongly heated in a reverberatory furnace, when $SO_2$ is driven off. The impure *work lead*, so formed, is purified by fusion in air, and removal of the film of oxids of Sn and Sb. If the ore be rich in Ag, that metal is extracted, by taking advantage of the greater fusibility of an alloy of Pb and Ag, than of Pb alone; and subsequent oxidation of the remaining Pb.

**Properties.**—*Physical.*—It is a bluish white metal; brilliant upon freshly cut surfaces; very soft and pliable; not very malleable or ductile; crystallizes in octahedra; a poor conductor of electricity; a better conductor of heat. When expanded by heat it does not, on cooling, return to its original volume.

*Chemical.*—When exposed to air it is oxidized, more readily and completely at high temperatures. The action of $H_2O$ on Pb varies with the conditions. Pure unaërated $H_2O$ has no action upon it. By the combined action of air and moisture Pb is oxidized, and the oxid dissolved in the $H_2O$, leaving a metallic surface for the continuance of the action. The solvent action of $H_2O$ upon Pb is increased, owing to the formation of basic salts, by the presence of nitrogenized organic substances, nitrates, nitrites, and chlorids. On the other hand, carbonates, sulfates, and phosphates, by their tendency to form insoluble coatings, diminish the corroding action of $H_2O$. Carbonic acid in small quantity, especially in presence of carbonates, tends to preserve Pb from solution, while $H_2O$ highly charged with it (soda water) dissolves the metal readily. Lead is dissolved, as a nitrate, by $HNO_3$.

$H_2SO_4$, when cold and moderately concentrated, does not affect it; but, when heated, dissolves it the more readily as the acid is more concentrated. It is attacked by HCl of sp. gr. 1.12, especially if heated. Acetic acid dissolves it as acetate, or, in the presence of $CO_2$, converts it into white lead.

**Oxids.—Lead Monoxid**—*Protoxid*—**Massicot**—**Litharge**—**Plumbi oxidum** (U. S.; Br.)—PbO—222.9—is prepared by heating Pb, or its carbonate, or nitrate, in air. If the product have been fused, it is **litharge**; if not, **massicot**. It forms copper-colored, mica-like plates, or a yellow powder; or crystallizes, from its solution in soda or potash, in white, rhombic dodecahedra, or in rose-colored cubes. It fuses near a red heat, and volatilizes at a white heat; sp. gr. 9.277–9.5. It is sparingly soluble in $H_2O$, forming an alkaline solution.

Heated in air to 300° (572° F.) it is oxidized to **minium**. It is readily reduced by H or C. With Cl it forms $PbCl_2$ and O. It is a strong base; decomposes alkaline salts, with liberation of the alkali. It dissolves in $HNO_3$, and in hot acetic acid, as nitrate or acetate. When ground up with oils it saponifies the glycerol ethers, the Pb combining with the fatty acids to form Pb soaps, one of which, **lead oleate**, is the **emplastrum plumbi** (U. S.; Br.). It also combines with the alkalies and earths to form **plumbites**. **Calcium plumbite**, $CaPb_2O_3$, is a crystalline salt, formed by heating PbO with milk of lime, and used in solution as a hair dye.

**Plumboso-plumbic Oxid**—*Red oxid*—**Minium**—**Red lead**—$Pb_3O_4$—684.7—is prepared by heating massicot to 300° (572° F.) in air. It ordinarily has the composition $Pb_3O_4$, and has been considered as composed of $PbO_2$, 2PbO; or as a basic lead salt of plumbic acid, $PbO_3Pb$, PbO. An orange-colored variety is formed when lead carbonate is heated to 300° (572° F.).

It is a bright red powder, sp. gr. 8.62. It is converted into PbO when strongly heated, or by the action of reducing agents. $HNO_3$ changes its color to brown, dissolving PbO and leaving $PbO_2$. It is decomposed by HCl, with formation of $PbCl_2$, $H_2O$ and Cl.

**Lead Dioxid.**—*Peroxid*, or *puce oxid*, or *brown oxid*, or *binoxid of lead*—*Plumbic anhydrid*—$PbO_2$—238.9—is prepared, either by dissolving the PbO out of red lead by dilute $HNO_3$, or by passing a current of Cl through $H_2O$, holding lead carbonate in suspension.

It is a dark, reddish brown, amorphous powder; sp. gr. 8.903–9.190; insoluble in $H_2O$. Heated, it loses half its O, and is converted into PbO. It is a valuable oxidant. It absorbs $SO_2$ to form $PbSO_4$. It combines with alkalies to form **plumbates**, $M_2PbO_3$.

**Plumbic Acid.**—$H_2PbO_3$—256.9—forms crystalline plates, at the +electrode, when alkaline solutions of the Pb salts are decomposed by a weak current.

**Lead Sulfid—Galena**—PbS—238.9—exists in nature. It is also formed by direct union of Pb and S; by heating PbO with S, or vapor of $CS_2$; or by decomposing a solution of a Pb salt by $H_2S$ or an alkaline sulfid.

The native sulfid is a bluish gray, and has a metallic luster; sp. gr. 7.58; that formed by precipitation is a black powder; sp. gr. 6.924. It fuses at a red heat and is partly sublimed, partly converted into a subsulfate. Heated in air it is converted into $PbSO_4$, PbO and $SO_2$. Heated in H it is reduced. Hot $HNO_3$ oxidizes it to $PbSO_4$. Hot HCl converts it into $PbCl_2$. Boiling $H_2SO_4$ converts it into $PbSO_4$ and $SO_2$.

**Lead Chlorid**—$PbCl_2$—277.9—is formed by the action of Cl upon Pb at a red heat; by the action of boiling HCl upon Pb, and by double decomposition between a lead salt and a chlorid.

It crystallizes in plates, or hexagonal needles; sparingly soluble in cold $H_2O$, less soluble in $H_2O$ containing HCl; more soluble in hot $H_2O$, and in concentrated HCl.

Several oxychlorids are known. **Cassel, Paris, Verona, or Turner's yellow** is $PbCl_2$, 7PbO.

**Lead Iodid—Plumbi iodidum** (U. S.; Br.)—$PbI_2$—460.09—is deposited, as a bright yellow powder, when a solution of potassium iodid is added to a solution of Pb salt. Fused in air, it is converted into an oxyiodid. Light and moisture decompose it, with liberation of I. It is almost insoluble in $H_2O$, soluble in solutions of ammonium chlorid, sodium hyposulfite, alkaline iodids, and potash.

**Salts of Lead.—Nitrates.—Lead Nitrate—Plumbi nitras** (U. S.; Br.)—$Pb(NO_3)_2$—330.9—is formed by solution of Pb, or of its oxids, in excess of $HNO_3$. It forms anhydrous crystals; soluble in $H_2O$. Heated, it is decomposed into PbO, O and $NO_2$.

Besides the neutral nitrate, basic lead nitrates are known, which seem to indicate the existence of nitrogen acids similar to those of phosphorus; $Pb_3(NO_4)_2$—**orthonitrate**; and $Pb_2N_2O_7$—**pyronitrate.**

**Lead Sulfate**—$PbSO_4$—302.9—is formed by the action of hot, concentrated $H_2SO_4$ on Pb; or by double decomposition between a sulfate and a Pb salt in solution. It is a white powder, almost insoluble in $H_2O$, soluble in concentrated $H_2SO_4$, from which it is deposited by dilution.

**Lead Chromate—Chrome yellow**—$PbCrO_4$—323.3—is formed by decomposing $Pb(NO_3)_2$ with potassium chromate. It is a yellow, amorphous powder, insoluble in $H_2O$, soluble in alkalies.

**Acetates.—Neutral Lead Acetate—Salt of Saturn—Sugar of Lead—Plumbi acetas** (U. S.; Br.)—$Pb(C_2H_3O_2)_2+3Aq$—324.9+54—is formed by dissolving PbO in acetic acid; or by exposing Pb in contact with acetic acid to air.

It crystallizes in large, oblique rhombic prisms, sweetish, with a

metallic after-taste; soluble in $H_2O$ and alcohol; its solutions being acid. In air it effloresces, and is superficially converted into carbonate. It fuses at 75.5° (167.9° F.); loses Aq and a part of its acid at 100° (212° F.), forming the sesquibasic acetate, $2[Pb(C_2H_3O_2)_2]Pb(OH)_2$; at 280° (536° F.) it enters into true fusion, and, at a slightly higher temperature, is decomposed into $CO_2$; Pb, and acetone. Its aqueous solution dissolves PbO, with formation of basic acetates.

**Sexbasic Lead Acetate**—$Pb(C_2H_3O_2)OH$, $2PbO$—728.7—is the main constituent of **Goulard's extract**=**Liq. plumbi subacetatis** (U. S.; Br.), and is formed by boiling a solution of the neutral acetate with PbO in fine powder. The solution becomes milky on addition of ordinary $H_2O$, from formation of the sulfate and carbonate.

**Lead Carbonate**—$PbCO_3$—266.9—occurs in nature as **cerusite**; and is formed, as a white, insoluble powder, when a solution of a Pb compound is decomposed by an alkaline carbonate, or by passing $CO_2$ through a solution containing Pb.

The **plumbi carbonas** (U. S.; Br.), or **white lead** or **ceruse**, is a basic carbonate $(PbCO_3)_2$, $PbH_2O_2$—774.7—mixed with varying proportions of other basic carbonates. It is usually prepared by the action of $CO_2$ on a solution of the subacetate, prepared by the action of acetic acid on Pb and PbO. It is a heavy, white powder, insoluble in $H_2O$, except in the presence of $CO_2$; soluble in acids with effervescence; and decomposed by heat into $CO_2$ and PbO. White lead enters into the composition of almost all oil-paints, being used to dilute other pigments. The darkening of oil-paintings is due to the formation of the black lead sulfid by atmospheric $H_2S$.

**Analytical Characters.**—(1) Hydrogen sulfid, in acid solution: a black ppt.; insoluble in alkaline sulfids, and in cold, dilute acids. (2) Ammonium sulfhydrate: black ppt.; insoluble in excess. (3) Hydrochloric acid: white ppt., in not too dilute solution; soluble in boiling $H_2O$. (4) Ammonium hydroxid: white ppt.; insoluble in excess. (5) Potash: white ppt.; soluble in excess, especially when heated. (6) Sulfuric acid: white ppt.; insoluble in weak acids, soluble in solution of ammonium tartrate. (7) Potassium iodid: yellow ppt.; sparingly soluble in boiling $H_2O$; soluble in large excess. (8) Potassium chromate: yellow ppt.; soluble in KHO solution. (9) Iron or zinc separate the element from solution of its salts.

**Action on the Economy.**—All the soluble compounds of Pb, and those which, although not soluble, are readily convertible into soluble compounds by $H_2O$, air, or the digestive fluids, are actively poisonous. Some are also injurious by their local action upon tissues with which they come in contact; such are the acetate, and, in less degree, the nitrate.

The **chronic** form of lead intoxication, **painter's colic**, etc., is purely poisonous, and is produced by the continued absorption of minute quantities of Pb, either by the skin, lungs, or stomach. The **acute** form presents symptoms referable to the local, as well as to the poisonous, action of the Pb salt, and is usually caused by the ingestion of a single dose of the acetate or carbonate.

Metallic Pb, although probably not poisonous of itself, causes chronic lead-poisoning by the readiness with which it is convertible into compounds capable of absorption. The principal sources of poisoning by metallic Pb are: the contamination of drinking water which has been in contact with the metal (see p. 73); the use of articles of food, or of chewing tobacco, which has been packed in tinfoil, containing an excess of Pb; the drinking of beer or other beverages which have been in contact with pewter; or the handling of the metal and its alloys.

Almost all the compounds of Pb may produce painter's colic. The carbonate, in painters, artists, manufacturers of white lead, and in persons sleeping in newly-painted rooms; the oxids, in the manufactures of glass, pottery, sealing-wax, and litharge, and by the use of lead-glazed pottery; by other compounds, by the inhalation of the dust of cloth factories, and by the use of lead hair-dyes.

Acute lead-poisoning is of by no means as common occurrence as the chronic form, and usually terminates in recovery. It is caused by the ingestion of a single large dose of the acetate, subacetate, carbonate, or of red lead. In such cases the administration of magnesium sulfate is indicated; it enters into double decomposition with Pb salt to form the insoluble $PbSO_4$.

Lead, once absorbed, is eliminated very slowly, it becoming fixed by combination with the proteins, a form of combination which is rendered soluble by potassium iodid. The channels of elimination are by the perspiration, urine and bile.

In the analysis for mineral poisons the major part of the Pb is precipitated as PbS in the treatment by $H_2S$. The PbS remains upon the filter after extraction with ammonium sulfhydrate. It is treated with warm HCl, which decolorizes it by transforming the sulfid into chlorid. The $PbCl_2$ thus formed is dissolved in hot $H_2O$, from which it crystallizes on cooling. The solution still contains $PbCl_2$ in sufficient quantity to respond to the tests for the metal.

Although Pb is not a normal constituent of the body, the everyday methods by which it may be introduced into the economy, and the slowness of its elimination, are such as to render the greatest caution necessary in drawing conclusions from the detection of Pb in the body after death.

## V. BISMUTH GROUP.

### BISMUTH.

*Symbol*=Bi—*Atomic weight*=208.5 (O=16:208.5; H=1:206.8)—*Molecular weight*=420 (?) —*Sp. gr.*=9.677–9.935—*Fuses at* 268° (514.4° F.).

This element is usually classed with Sb; by some writers among the metals, by others in the phosphorus group. We are led to class Bi in our third class, and in a group alone, because: (1) while the so-called salts of Sb are not salts of the element, but of the radical $(SbO)'$, *antimonyl*, Bi enters into saline combination, not only in the radical bismuthyl $(BiO)'$, but also as an element; (2) while the compounds of the elements of the N group in which those elements are quinquivalent are, as a rule, more stable than those in which they are trivalent, Bi is trivalent in all its known compounds except one, which is very unstable, in which it is quinquivalent; (3) the hydrates of the N group are strongly acid, and their corresponding salts are stable and well defined; but those hydrates of Bi which are acid are but feebly so, and the bismuthates are unstable; (4) no compound of Bi and H is known.

**Occurrence.**—Occurs principally free, also as $Bi_2O_3$ and $Bi_2S_3$.

**Properties.**—Crystallizes in brilliant, metallic rhombohedra; hard and brittle.

It is only superficially oxidized in cold air. Heated to redness in air, it becomes coated with a yellow film of oxid. In $H_2O$, containing $CO_2$, it forms a crystalline subcarbonate. It combines directly with Cl, Br and I. It dissolves in hot $H_2SO_4$ as sulfate, and in $HNO_3$ as nitrate.

It is usually contaminated with As, from which it is best purified by heating to redness a mixture of powdered bismuth, potassium carbonate, soap and charcoal, under a layer of charcoal. After an hour the mass is cooled; the button is separated and fused until its surface begins to be coated with a yellowish brown oxid.

**Oxids.**—Four oxids are known: $Bi_2O_2$, $Bi_2O_3$, $Bi_2O_4$, and $Bi_2O_5$.

**Bismuth Trioxid**—*Bismuthous oxid*—*Protoxid*—$Bi_2O_3$—465—is formed by heating Bi, or its nitrate, carbonate or hydrate. It is a pale yellow, insoluble powder; sp. gr. 8.2; fuses at a red heat; soluble in HCl, $HNO_3$ and $H_2SO_4$ and in fused potash.

**Hydrates.**—Bismuth forms at least four hydrates.

**Bismuthous Hydroxid**—$BiH_3O_3$—259.5—is formed, as a white precipitate, when potash or ammonium hydroxid is added to a cold

solution of a Bi salt. When dried it loses $H_2O$, and is converted into **Bismuthyl hydroxid** $(BiO)HO$.

**Bismuthic acid**—$(BiO_2)HO$—257.5—is deposited, as a red powder, when Cl is passed through a boiling solution of potash, holding bismuthous hydroxid in suspension. When heated it is converted into the **pentoxid,** $Bi_2O_5$.

**Pyrobismuthic Acid**—$H_4Bi_2O_7$—533—is a dark brown powder, precipitated from solution of bismuth nitrate by potassium cyanid.

**Bismuth Trichlorid**—*Bismuthous chlorid*—$BiCl_3$—314.9—is formed by heating Bi in Cl; by distilling a mixture of Bi and mercuric chlorid; or by distilling a solution of Bi in aqua regia. It is a fusible, volatile, deliquescent solid; soluble in dilute HCl. On contact with $H_2O$ it is decomposed with formation of **bismuthyl chlorid,** $(BiO)Cl$, or **pearl white.**

**Bismuth Nitrate**—$Bi(NO_3)_3+5$ Aq—394.5+90—obtained by dissolving Bi in $HNO_3$. It crystallizes in large, colorless prisms; at 150° (302° F.), or by contact with $H_2O$, it is converted into bismuthyl nitrate; at 260° (500° F.) into $Bi_2O_3$.

**Bismuthyl Nitrate**—*Trisnitrate* or *subnitrate of bismuth*—*Flake white*—**Bismuthi subnitras**—(U. S.; Br.)—$(BiO)NO_3H_2O$—304.5—is formed by decomposing a solution of $Bi(NO_3)_3$ with a large quantity of $H_2O$. It is a white, heavy, faintly acid powder; soluble to a slight extent in $H_2O$ when freshly precipitated, the solution depositing it again on standing. It is decomposed by pure $H_2O$, but not by $H_2O$ containing $\frac{1}{500}$ ammonium nitrate. It usually contains 1 Aq, which it loses at 100° (212° F.) Bismuth subnitrate, as well as the subcarbonate, is liable to contamination with arsenic, which accompanies bismuth in its ores.

**Bismuthyl Carbonate**—**Bismuth subcarbonate**—**Bismuthi subcarbonas** (U. S.) **Bismuthi carbonas** (Br.)—$(BiO)_2CO_3H_2O$—527—is a white or yellowish, amorphous powder, formed when a solution of an alkaline carbonate is added to a solution of $Bi(NO_3)_3$. It is odorless, tasteless, and insoluble in $H_2O$ and in alcohol.

When heated to 100° (212° F.), it loses $H_2O$, and is converted into $(BiO)_2CO_3$. At a higher temperature it is further decomposed into $Bi_2O_3$ and $CO_2$.

**Analytical Characters.**—(1) Water: white ppt., even in presence of tartaric acid, but not of $HNO_3$, HCl, or $H_2SO_4$. (2) Hydrogen sulfid: black ppt., insoluble in dilute acids and in alkaline sulfids. (3) Ammonium sulfhydrate: black ppt., insoluble in excess. (4) Potash soda, or ammonia: white ppt., insoluble in excess, and in tartaric acid; turns yellow when the liquid is boiled. (5) Potassium ferrocyanid: yellowish ppt., insoluble in HCl. (6) Potassium ferricyanid: yellowish ppt., soluble in HCl. (7) Infusion of galls:

orange ppt. (8) Potassium iodid: brown ppt., soluble in excess. (9) Reacts with Reinsch's test (*q. v.*), but gives no sublimate in the glass tube.

**Action on the Economy.**—Although the medicinal compounds of bismuth are probably poisonous, if taken in sufficient quantity, the ill effects ascribed to them are in most, if not all cases, referable to contamination with arsenic. Symptoms of arsenical poisoning have been frequently observed when the subnitrate has been taken internally, and also when it has been used as a cosmetic. Bismuth subnitrate is frequently administered by physicians in cases of arsenical poisoning, not recognized as such during life.

When preparations of bismuth are administered, the alvine discharges contain bismuth sulfid, as a dark brown powder.

## VI. TIN GROUP.

### TITANIUM—ZIRCONIUM—TIN.

Ti and Sn are bivalent in one series of compounds, $SnCl_2$, and quadrivalent in another, $SnCl_4$. Zr, so far as known, is always quadrivalent. Each of these elements forms an acid (or salts corresponding to one) of the composition of $H_2MO_3$, and a series of oxysalts of the composition of $M^{iv}(NO_3)_4$.

### TITANIUM.

*Symbol*=Ti—*Atomic weight*=48—*Sp. gr.*=5.3.

Occurs in clays and iron ores, and as $TiO_2$ in several minerals. **Titanic anhydrid**, $TiO_2$, is a white, insoluble, infusible powder, used in the manufacture of artificial teeth; dissolves in fused KHO, as potassium titanate. Titanium combines readily with N, which it absorbs from air when heated. When $NH_3$ is passed over red-hot $TiO_2$, it is decomposed with formation of the violet nitrid, $TiN_2$. Another compound of Ti and N forms hard, copper-colored, cubical crystals.

### ZIRCONIUM.

*Symbol*=Zr—*Atomic weight*=89—*Sp. gr.*=4.15.

Occurs in zircon and hyacinth. Its oxid, **zirconia**, $ZrO_2$, is a white powder, insoluble in KHO. Being infusible, and not altered by exposure to air, it is used in pencils to replace lime in the calcium light.

## TIN.

*Symbol*=Sn (*Stannum*) —*Atomic weight*=118.5 (O=16:118.5; H=1:117.55)—*Molecular weight*=235.4 (?)—*Sp. gr.*=7.285–7.293—*Fuses at* 228° (442.4° F.).

**Occurrence.**—As **tinstone** ($SnO_2$) or **cassiterite**, and in **stream tin.**

**Preparation.**—The commercial metal is prepared by roasting the ore, extracting with $H_2O$, reducing the residue by heating with charcoal, and refining.

**Pure tin** is obtained by dissolving the metal in HCl; filtering; evaporating; dissolving the residue in $H_2O$: decomposing with ammonium carbonate; and reducing the oxid with charcoal.

**Properties.**—A soft, malleable, bluish white metal; but slightly tenacious; emits a peculiar sound, the **tin-cry**, when bent. A good conductor of heat and electricity. Air affects it but little, except when it is heated; more rapidly if Sn be alloyed with Pb. It oxidizes slowly in $H_2O$; more rapidly in the presence of sodium chlorid. Its presence with Pb accelerates the action of $H_2O$ upon the latter. It dissolves in HCl as $SnCl_2$. In presence of a small quantity of $H_2O$, $HNO_3$ converts it into metastannic acid. Alkaline solutions dissolve it as metastannates. It combines directly with Cl, Br, I, S, P and As.

**Tin plates** are thin sheets of Fe, coated with Sn. **Tin foil** consists of thin laminæ of Sn, frequently alloyed with Pb. Copper and iron vessels are **tinned** after brightening, by contact with molten Sn. Pewter, bronze, bell metal, gun metal, britannia metal, speculum metal, type metal, solder, and fusible metal, contain Sn.

**Oxids.— Stannous Oxid**—*Protoxid* — SnO —134.5— obtained by heating the hydroxid or oxalate without contact of air. It is a white, amorphous powder, soluble in acids, and in hot, concentrated solution of potash. It absorbs O readily.

**Stannic Oxid**—*Binoxid of tin*—$SnO_2$—150.5—occurs native as *tinstone* or *cassiterite*, and is formed when Sn or SnO is heated in air. It is used as a polishing material, under the name of **putty powder.**

**Hydrates.** — **Stannous Hydroxid** — $SnH_2O_2$ —152.5 — is a white precipitate, formed by alkaline hydroxids and carbonates in solutions of $SnCl_2$.

**Stannic Acid**—$H_2SnO_3$—168.5—is formed by the action of alkaline hydroxids on solutions of $SnCl_4$. It dissolves in solutions of the alkaline hydroxids, forming **stannates.**

**Metastannic Acid**—$H_2Sn_5O_{11}$—770.5—is a white, insoluble powder, formed by acting on Sn with $HNO_3$.

**Chlorids.** — **Stannous Chlorid** — *Protochlorid* — **Tin crystals**— $SnCl_2+2$ Aq —189.4+36— is obtained by dissolving Sn in HCl. It

crystallizes in colorless prisms; soluble in a small quantity of $H_2O$; decomposed by a large quantity, unless in the presence of free HCl, with formation of an oxychlorid. Loses its Aq at 100° (212° F.). In air it is transformed into stannic chlorid and oxychlorid. Oxidizing and chlorinating agents convert it into $SnCl_4$. It is a strong reducing agent.

**Stannic Chlorid**—*Bichlorid—Liquid of Libavius*—$SnCl_4$—260.3—is formed by acting on Sn or $SnCl_2$ with Cl, or by heating Sn in aqua regia. It is a fuming, yellowish liquid; sp. gr. 2.28; boils at 120° (248° F.).

**Analytical Characters.**—STANNOUS.—(1) Potash or soda: white ppt.; soluble in excess; the solution deposits Sn when boiled. (2) Ammonium hydroxid: white ppt; insoluble in excess; turns olive-brown when the liquid is boiled. (3) Hydrogen sulfid: dark brown ppt.; soluble in KHO, alkaline sulfids, and hot $H_2O$. (4) Mercuric chlorid: white ppt., turning gray and black. (5) Auric chlorid: purple or brown ppt., in presence of small quantities of $HNO_3$. (6) Zinc: deposit of Sn.

STANNIC.—(1) Potash or ammonia: white ppt.; soluble in excess. (2) Hydrogen sulfid: yellow ppt.; soluble in alkalies, alkaline sulfids, and hot HCl. (3) Sodium hyposulfite: yellow ppt., when heated.

## VII. PLATINUM GROUP.

PALLADIUM. PLATINUM.

## VIII. RHODIUM GROUP.

RHODIUM. RUTHENIUM. IRIDIUM

The elements of these two groups, together with osmium, are usually classed as "metals of the platinum ores." They all form hydrates (or salts representing them) having acid properties. Osmium has been removed, because the relations existing between its compounds, and those of molybdenum and tungsten, are much closer than those which they exhibit to the compounds of these groups. The separation of the remaining platinum metals into two groups is based upon resemblances in the composition of their compounds, as shown in the following table.

| | | CHLORIDS. | | |
|---|---|---|---|---|
| $PdCl_2$ | $PtCl_2$ | $RhCl_2$ | $RuCl_2$ | ? |
| $PdCl_4$ | $PtCl_4$ | —— | $RuCl_4$ | $IrCl_4$ |
| —— | —— | $Rh_2Cl_6$ | $Ru_2Cl_6$ | $Ir_2Cl_6$ |

OXIDS.

| | | |
|---|---|---|
| PdO . . . . . PtO | RhO . . . . . RuO . . . . . IrO | |
| —— . . . . . —— | $Rh_2O_3$ . . . . . $Ru_2O_3$ . . . . . $Ir_2O_3$ | |
| $PdO_2$ . . . . . $PtO_2$ | $RhO_2$ . . . . . $RuO_2$ . . . . . $IrO_2$ | |
| —— . . . . . —— | $RhO_3$ . . . . . $RuO_3$ . . . . $IrO_3$ | |
| —— . . . . . —— | —— . . . . . $RuO_4$ . . . —— | |

## PLATINUM.

*Symbol*=Pt—*Atomic weight*=194.8 (O=16:194.8; H=1:193.25) —*Molecular weight*=390 (?)—*Sp. gr.*=21.1-21.5.

**Occurrence.**—Free and alloyed with Os, Ir, Pd, Rh, Ru, Fe, Pb, Au, Ag, and Cu.

**Properties.**—The compact metal has a silvery luster; softens at a white heat; may be welded; fuses with difficulty; highly malleable, ductile and tenacious. **Spongy platinum** is a grayish, porous mass, formed by heating the double chlorid of Pt and $NH_4$. **Platinum black** is a black powder, formed by dissolving $PtCl_2$ in solution of potash, and heating with alcohol. Both platinum black and platinum sponge are capable of condensing large quantities of gas, and act as indirect oxidants.

Platinum is not oxidized by air or O; it combines directly with Cl, P, As, Si, S, and C; is not attacked by acids, except aqua regia, in which it dissolves as $PtCl_4$. It forms fusible alloys when heated with metals or reducible metallic oxids. It is attacked by mixtures liberating Cl, and by contact with heated phosphates, silicates, hydroxids, nitrates, or carbonates of the alkaline metals.

**Platinic chlorid**—*Tetrachlorid* or *perchlorid of platinum*—$PtCl_4$ —336.6—is obtained by dissolving Pt in aqua regia, and evaporating. It crystallizes in very soluble, deliquescent, yellow needles. Its solution is used as a test for compounds of $NH_4$ and K.

## CLASS IV.—BASYLOUS ELEMENTS.

**Elements whose Oxids unite with Water to form Bases; never to form Acids. Which form Oxysalts.**

# I. SODIUM GROUP.

**Alkali Metals.**

LITHIUM—SODIUM—POTASSIUM—RUBIDIUM—CÆSIUM—SILVER.

Each of the elements of this group forms a single chlorid, M′Cl, and one or more oxids, the most stable of which has the composition $M'_2O$. They are, therefore, univalent. Their hydroxids, M′HO, are more or less alkaline and have markedly basic characters. Silver resembles the other members of the group in chemical properties, although it does not in physical characters.

The name "alkali," first applied to "potash" from wood ashes (p. 178) is now used to designate substances which are strongly basic, are alkaline in reaction, and saponify fats. The **caustic alkalies** are the hydroxids of K and Na, the **carbonated alkalies** are their carbonates. **Volatile alkali** is ammonium hydroxid or carbonate.

## LITHIUM.

*Symbol*=Li—*Atomic weight*=7 (O=16:7.03; H=1:6.97)—*Molecular weight*=14 (?)—*Sp. gr.*=0.589—*Fuses at* 180° (356° F.)—*Discovered by Arfvedson in* 1817—*Name from* λίθειος=stony.

**Occurrence.**—Widely distributed in small quantity; in many minerals and mineral waters; in the ash of tobacco and other plants; in the milk and blood.

**Properties.**—A silver-white, ductile, volatile metal; the lightest of the solid elements; burns in air with a crimson flame; decomposes $H_2O$ at ordinary temperatures, without igniting.

**Lithium Oxid**—$Li_2O$—30—is a white solid, formed by burning Li in dry O. It dissolves slowly in $H_2O$ to form **lithium hydroxid**—LiHO.

**Lithium Chlorid**—LiCl—43.5—crystallizes in deliquescent, regular octahedra; very soluble in $H_2O$ and in alcohol.

**Lithium Bromid**—**Lithii bromidum**—(U. S.)—LiBr—87—is formed by decomposing lithium sulfate with potassium bromid; or by saturating a solution of HBr with lithium carbonate. It crystallizes in very deliquescent, soluble needles.

**Lithium Carbonate**—**Lithii carbonas** (U. S.; Br.)—$Li_2CO_3$—74—

is a white, sparingly soluble, alkaline, amorphous powder. With uric acid it forms lithium urate (q. v.).

**Analytical Characters.**—(1) Ammonium carbonate: white ppt. in concentrated solutions; not in dilute solutions, or in presence of ammoniacal salts. (2) Sodium phosphate: white ppt. in neutral or alkaline solution; soluble in acids and in solutions of ammoniacal salts. (3) It colors the Bunsen flame red; and exhibits a spectrum of two lines—$\lambda$=6705 and 6102 (Fig. 14, No. 4, p. 22).

## SODIUM.

*Symbol* = Na (*Natrium*)—*Atomic weight* = 23 (O = 16:23.05; H=1:22.87)—*Molecular weight*=46 (?)—*Sp. gr.*=0.972—*Fuses at* 95.6° (204.1° F.)—*Boils at* 742° (1368° F.)—*Discovered by Davy*, 1807.

**Occurrence.**—As chlorid, very abundantly and widely distributed; also as carbonate, nitrate, sulfate, borate, etc.

**Preparation.**—By heating a mixture of dry sodium carbonate, chalk, and charcoal to whiteness in iron retorts, connected with suitable condensers, in which the distilled metal collects, under a layer of coal naphtha. It is now manufactured by the electrolysis of fused NaHO.

**Properties.**—A silver-white metal, rapidly tarnished, and coated with a yellow film in air. Waxy at ordinary temperatures; volatile at a white heat, forming a colorless vapor, which burns in air with a yellow flame.

In air it is gradually oxidized from the surface, but may be kept in closed vessels, without the protection of a layer of naphtha. It decomposes $H_2O$, sometimes explosively. Burns with a yellow flame. Combines directly with Cl, Br, I, S, P, As, Pb, and Sn.

**Oxids.**—Two oxids are known: **Sodium monoxid**—$Na_2O$—a grayish white mass; formed when Na is burnt in dry air, or by the action of Na on NaHO. **Sodium dioxid**—$Na_2O_2$—a white solid, formed when Na is heated in dry air to 200° (392° F.). Sodium dioxid, or peroxid, is now manufactured by oxidizing the fused metal in dry air or oxygen, and is used as a bleaching and oxidizing agent. It is a yellowish white, amorphous, very hygroscopic powder. If the temperature be kept low it dissolves in dilute acids, forming a strong solution of hydrogen peroxid: $Na_2O_2+2HCl=2NaCl+H_2O_2$. With water it produces a great elevation of temperature and liberates nascent oxygen: $2Na_2O_2+2H_2O=4NaHO+O_2$. With magnesium sulfate it forms magnesium peroxid, a non-alkaline oxydant: $Na_2O_2+MgSO_4=Na_2SO_4+MgO_2$.

**Sodium Hydroxid**—*Sodium hydrate*—**Caustic Soda**—**Soda** (U.S.) —**Soda caustica** (Br.)—NaHO—40—is formed: (1) When $H_2O$ is decomposed by Na; (2) by decomposing sodic carbonate by calcium hydroxid: $Na_2CO_3+CaH_2O_2=CO_3Ca+2NaHO$ (soda by lime); (3) in the same manner as in (2), using barium hydroxid in place of lime (soda by baryta). It frequently contains considerable quantities of As. (4) Caustic soda is now largely manufactured by electrolytic decomposition of NaCl. The Castner process is the one usually adopted. In it, by a rocking arrangement, mercury, as the cathode, first takes up the liberated sodium, and is then brought in contact with a suitable quantity of water. The reactions are: $2NaCl=Na_2+Cl_2$, and $Na_2+2H_2O=2NaHO+H_2$. (See Chlorin.)

It is an opaque, white, fibrous, brittle solid; fusible below redness; sp. gr. 2.00; very soluble in $H_2O$, forming strongly alkaline and caustic solutions (**soda lye** and **liq. sodæ**). When exposed to air, solid or in solution, it absorbs $H_2O$ and $CO_2$, and is converted into carbonate. Its solutions attack glass.

**Sodium Chlorid**—**Common salt**—**Sea salt**—**Table salt**—**Sodii chloridum** (U. S.; Br.)—NaCl—58.5—occurs very abundantly in nature, deposited in the solid form as **rock salt**; in solution in all natural waters, especially in sea and mineral spring waters; in suspension in the atmosphere; and as a constituent of almost all animal and vegetable tissues and fluids. It is formed in an infinite variety of chemical reactions. It is obtained from rock salt, or from the waters of the sea, or of saline springs; and is the source from which all the Na compounds are usually obtained, directly or indirectly.

It crystallizes in anhydrous, white cubes, or octahedra; sp. gr. 2.078; fuses at a red heat, and crystallizes on cooling; sensibly volatile at a white heat; quite soluble in $H_2O$, the solubility varying but slightly with the variations of temperature. Dilute solutions yield almost pure ice on freezing. It is precipitated from concentrated solutions by HCl. It is insoluble in absolute alcohol; sparingly soluble in dilute spirit. It is decomposed by $H_2SO_4$ with formation of HCl and sodium sulfate: $2NaCl+H_2SO_4=2HCl+Na_2SO_4$.

**Sodium Bromid**—**Sodii bromidum** (U. S.)—NaBr—103—is formed by dissolving Br in solution of NaHO to saturation; evaporating; calcining at dull redness; redissolving, filtering, and crystallizing. It crystallizes in anhydrous cubes; quite soluble in $H_2O$, soluble in alcohol.

**Sodium Iodid**—**Sodii iodidum** (U. S.)—NaI—150—is prepared by heating together $H_2O$, Fe, and I in fine powder; filtering; adding an equivalent quantity of sodium sulfate, and some slacked lime, boiling, decanting and evaporating. Crystallizes in anhydrous cubes; very soluble in $H_2O$; soluble in alcohol.

**Sodium Nitrate—Cubic or Chili saltpeter—Sodii nitras** (U. S.); **Sodæ nitras** (Br.)—$NaNO_3$—85—occurs in natural deposits in Chili and Peru. It crystallizes in anhydrous, deliquescent rhombohedra; cooling and somewhat bitter in taste; fuses at 310° (590° F.); very soluble in $H_2O$. Heated with $H_2SO_4$, it is decomposed, yielding $HNO_3$ and hydrosodic sulfate: $H_2SO_4+NaNO_3=HNaSO_4+HNO_3$. This reaction is that used for obtaining $HNO_3$.

**Sulfates.—Monosodic Sulfate**—*Hydrosodic sulfate—Acid sodium sulfate—Bisulfate*—$HNaSO_4$—120—crystallizes in long, four-sided prisms; is unstable and decomposed by air, $H_2O$ or alcohol, into $H_2SO_4$ and $Na_2SO_4$. Heated to dull redness it is converted into **sodium pyrosulfate**, $Na_2S_2O_7$, corresponding to Nordhausen sulfuric acid.

**Disodic Sulfate**—*Sodic sulfate—Neutral sodium sulfate*—**Glauber's salt—Sodii sulfas** (U. S.); **sodæ sulfas** (Br.)—$Na_2SO_4+n$Aq—142 $+n$ 18—occurs in nature in solid deposits, and in solution in natural waters. It is obtained as a secondary product in the manufacture of HCl, by the action of $H_2SO_4$ on NaCl, the decomposition occurring according to the equation: $2NaCl+H_2SO_4=Na_2SO_4+2\,HCl$, if the temperature be raised sufficiently. At lower temperatures, the monosodic salt is produced, with only half the yield of HCl: $NaCl+H_2SO_4=NaHSO_4+HCl$.

It crystallizes with 7 Aq, from saturated or supersaturated solutions at 5° (41° F.); or, more usually, with 10 Aq. As usually met with it is in large, colorless, oblique, rhombic prisms with 10 Aq; which effloresce in air, and gradually lose all their Aq. It fuses at 33° (91.4° F.) in its Aq, which it gradually loses. If fused at 33° (91.4° F.), and allowed to cool, it remains liquid in *supersaturated* solution, from which it is deposited, the entire mass becoming solid, on contact with a small particle of solid matter. It dissolves in HCl with considerable diminution of temperature.

**Sodium Sulfite—Sodii sulfis** (U. S.)—$Na_2SO_3+7$ Aq—126+126—is formed by passing $SO_2$ over crystallized $Na_2CO_3$. It crystallizes in efflorescent, oblique prisms; quite soluble in $H_2O$, forming an alkaline solution. It acts as a reducing agent.

**Sodium Thiosulfate**—*Sodium hyposulfite*—**Sodii hyposulfis** (U. S.)—$Na_2S_2O_3+5$ Aq—158+90—is obtained by dissolving S in hot concentrated solution of $Na_2SO_3$, and crystallizing.

It forms large, colorless, efflorescent prisms; fuses at 45° (113° F.); very soluble in $H_2O$, insoluble in alcohol. Its solutions precipitate alumina from solutions of Al salts, without precipitating Fe or Mn; they dissolve many compounds insoluble in $H_2O$; cuprous hydroxid, iodids of Pb, Ag and Hg, sulfids of Ca and Pb. It acts as a disinfectant and antiseptic. $H_2SO_4$ decomposes $Na_2S_2O_3$ according

to the equation: $Na_2S_2O_3+H_2SO_4=Na_2SO_4+SO_2+S+H_2O$; and most other acids behave similarly. Oxalic, and a few other acids, decompose the thiosulfate with formation of $H_2S$ as well as $SO_2$ and S.

**Silicates.**—Quite a number of silicates of Na are known. If silica and $Na_2CO_3$ be fused together, the residue extracted with $H_2O$, and the solution evaporated, a transparent, glass-like mass, soluble in warm water, remains; this is **soluble glass** or **water glass.** Exposed to air in contact with stone, it becomes insoluble, and forms an impermeable coating.

**Phosphates.**—**Trisodic Phosphate**—*Basic sodium phosphate*—$Na_3PO_4+12$ Aq—164+216—is obtained by adding NaHO to disodic phosphate solution, and crystallizing. It forms six-sided prisms; quite soluble in $H_2O$. Its solution is alkaline, and, on exposure to air, absorbs $CO_2$, with formation of $HNa_2PO_4$ and $Na_2CO_3$.

**Disodic Phosphate**—*Hydro-disodic phosphate*—*Neutral sodium phosphate*—*Phosphate of soda*—**Sodii phosphas** (U. S.); **sodæ phosphas** (Br.)—$HNa_2PO_4+12$ Aq—142+216—is obtained by converting tricalcic phosphate into monocalcic phosphate, and decomposing that salt with sodium carbonate: $Ca(PO_4H_2)_2+2Na_2CO_3=CaCO_3+H_2O+CO_2+2HNa_2PO_4$.

Below 30° (86° F.) it crystallizes in oblique rhombic prisms, with 12 Aq; at 33° (91.4° F.) it crystallizes with 7 Aq. The salt with 12 Aq effloresces in air, and parts with 5 Aq; and is very soluble in $H_2O$. The salt with 7 Aq is not efflorescent, and less soluble in $H_2O$. Its solutions are faintly alkaline.

**Monosodic Phosphate**—*Acid sodium phosphate*—$H_2NaPO_4+$ Aq—120+18—crystallizes in rhombic prisms; forming acid solutions. At 100° (212° F.) it loses Aq; at 200° (392° F.) it is converted into **acid pyrophosphate**, $Na_2H_2P_2O_7$; and at 204° (399.2° F.) into the **metaphosphate**, $NaPO_3$.

**Sodium Arsenites.**—The disodic arsenite, $Na_2HAsO_3$, is obtained as a viscous mass by fusing together 1 molecule of $As_2O_3$ and 2 molecules of $Na_2CO_3$ without contact of air. The monosodic arsenite, $NaH_2AsO_3$, is formed when an aqueous solution of $Na_2CO_3$ is boiled with $As_2O_3$. By prolonged boiling this is converted into the pyroarsenite, $Na_2H_2As_2O_5$, and this into the metarsenite, $NaAsO_2$, by progressive loss of water. Sodium arsenites exist in embalming liquids and are used in dyeing.

**Sodium Arsenates.**—The three arsenates, $NaH_2AsO_4$, $Na_2HAsO_4$ and $Na_3AsO_4$ corresponding to the phosphates, are known, and are used in dyeing processes,

**Disodic Tetraborate**—*Sodium pyroborate*—*Borate of sodium*—**Borax**—*Tincal*—**Sodii boras** (U. S.); **Borax** (Br.)—$Na_2B_4O_7+10$ Aq—202+180—is prepared by boiling boric acid with $Na_2CO_3$ and crys-

tallizing. It crystallizes in hexagonal prisms with 10 Aq; permanent in moist air, but efflorescent in dry air; or in regular octahedra with 5 Aq, permanent in dry air. Either form, when heated, fuses in its Aq, swells considerably; at a red heat becomes anhydrous; and, on cooling, leaves a transparent, glass-like mass. When fused it is capable of dissolving many metallic oxids, forming variously colored masses, hence its use as a flux and in blow-pipe analysis.

**Sodium Hypochlorite**—NaClO—74.5—only known in solution—**Liq. sodæ chloratæ** (U. S.; Br.) or **Labarraque's solution**—obtained by decomposing a solution of chlorid of lime by $Na_2CO_3$. It it a valuable source of Cl, and is used as a bleaching and disinfecting agent.

**Sodium Chlorate**—**Sodii chloras** (U. S.)—$NaClO_3$—106.5—is manufactured industrially by treating milk of lime with Cl. The solution of calcium chlorid and chlorate so obtained is treated with $Na_2SO_4$, after removal of part of the $CaCl_2$ by concentration and cooling to 12° (53.6° F.). The $NaClO_3$ and NaCl formed are separated by taking advantage of the greater solubility of the former. $NaClO_3$ is soluble in its own weight of $H_2O$ at 20° (68° F.).

**Sodium Manganate**—$Na_2MnO_4$+10 Aq—164+180—faintly colored crystals, forming a green solution with $H_2O$—**Condy's green disinfectant.**

**Sodium Permanganate**—$Na_2Mn_2O_8$—282—prepared in the same way as the K salt (*q. v.*), which it resembles in its properties. It enters into the composition of **Condy's fluid,** and of "**chlorozone,**" which contains $Na_2Mn_2O_8$ and NaClO.

**Sodium Acetate**—**Sodii acetas** (U. S.); **Sodæ acetas** (Br.)—$NaC_2H_3O_2$+3 Aq—82+54—crystallizes in large, colorless prisms; acid and bitter in taste; quite soluble in $H_2O$, soluble in alcohol; loses its Aq in dry air, and absorbs it again from moist air. Heated with soda lime, it yields marsh gas. The anhydrous salt, heated with $H_2SO_4$, yields glacial acetic acid.

**Carbonates.**—Three are known: $Na_2CO_3$, $HNaCO_3$, and $H_2Na_4(CO_3)_3$.

**Disodic Carbonate**—*Neutral Carbonate*—*Soda*—**Sal soda**—**Washing Soda**—**Soda crystals**—**Sodii carbonas** (U. S.); **Sodæ carbonas** (Br.)—$Na_2CO_3$+10 Aq—106+180—industrially the most important of the Na compounds, is manufactured by Leblanc's or Solvay's processes; or from *cryolite*, a native fluorid of Na and Al.

Leblanc's process, in its present form, consists of three distinct processes: (1) The conversion of NaCl into the sulfate, by decomposition by $H_2SO_4$. (2) The conversion of the sulfate into carbonate, by heating a mixture of the sulfate with calcium carbonate and charcoal. The product of this reaction, known as **black ball soda,** is a

mixture of sodium carbonate with charcoal and calcium sulfid and oxid. (3) The purification of the product obtained in (2). The ball black is broken up, disintegrated by steam, and lixiviated. The solution on evaporation yields the **soda salt** or **soda** of commerce.

Of late years Leblanc's process has been in great part replaced by Solvay's method, or the *ammonia process*, which is more economical, and yields a purer product. In this process sodium chlorid and ammonium bicarbonate react upon each other, with production of the sparingly soluble sodium bicarbonate, and the very soluble ammonium chlorid. The sodium bicarbonate is then simply collected, dried, and heated, when it is decomposed into $Na_2CO_3$, $H_2O$, and $CO_2$. Sodium carbonate is also made from cryolite, a double fluorid of sodium and aluminium found in Greenland. This is heated with limestone when: $Al_2Na_6F_{12}+6CaCO_3=6CaF_2+6CO_2+Na_6Al_2O_6$. The sodium aluminate is extracted with water and the solution treated with carbon dioxid (obtained in the first reaction) when: $Na_6Al_2O_6+3H_2O+3CO_2=3Na_2CO_3+Al_2(OH)_6$.

The anhydrous carbonate, *Sodii carbonas exsiccatus* (U. S.), $Na_2CO_3$, is formed, as a white powder, by calcining the crystals. It fuses at dull redness, and gives off a little $CO_2$. It combines with and dissolves in $H_2O$ with elevation of temperature.

The crystalline sodium carbonate, $Na_2CO_3+10Aq$, forms large rhombic crystals, which effloresce rapidly in dry air; fuse in their Aq at 34° (93.2° F.); are soluble in $H_2O$, most abundantly at 38° (100.4° F.). The solutions are alkaline in reaction.

**Monosodic Carbonate**—*Hydrosodic carbonate*—**Bicarbonate of soda**—*Acid carbonate of soda*—*Vichy salt*—**Sodii bicarbonas** (U. S.)—**Sodæ bicarbonas** (Br.)—$NaHCO_3$—84—exists in solution in many mineral waters. It is obtained by the action of $CO_2$ upon the disodic salt in the presence of $H_2O$; or, as above described, by the Solvay method.

It crystallizes in rectangular prisms, anhydrous and permanent in dry air. In damp air it gives off $CO_2$, and is converted into the **sesquicarbonate**, $Na_4H_2(CO_3)_3$. When heated it gives off $CO_2$ and $H_2O$, and leaves the disodic carbonate. Quite soluble in water; above 70° (158° F.) the solution gives off $CO_2$. The solutions are alkaline.

**Analytical Characters.**—(1) Hydrofluosilicic acid: gelatinous ppt., if not too dilute. (2) Potassium pyroantimonate, in neutral solution, and in absence of metals other than K and Li: a white, flocculent ppt.; becoming crystalline on standing. (3) Periodic acid in excess: white ppt., in not too dilute solutions. (4) Colors the Bunsen flame yellow, and shows a brilliant double line at $\lambda$=5895 and 5889 (Fig. 14, No. 2, p. 22).

## POTASSIUM.

*Symbol* = K (*Kalium*)—*Atomic weight* = 39 (O = 16 : 39.15 ; H = 1 : 38.84)—*Molecular weight* = 78 (?)—*Sp. gr.* = 0.865—*Fuses at* 62.5° (144.5° F.)—*Boils at* 667° (1233° F.)—*Discovered by Davy*, 1807—*Names from* pot ash, *and* Kali = ashes (Arabic).

Potassium silicates are widely distributed in rocks and minerals. The ash of plants contain about 10 per cent. of potassium carbonate, and this was formerly the chief source of the K compounds. Almost all of these are now derived from the deposits of **carnallite**: KCl, $MgCl_2$+6Aq, and allied minerals at Stassfurt in Germany.

It is prepared by a process similar to that followed in obtaining Na; is a silver-white metal; brittle at 0° (32° F.); waxy at 15° (59° F.); fuses at 62.5° (144.5° F.); distils in green vapors at a red heat, condensing in cubic crystals. It is also obtained by electrolysis of fused KHO.

It is the only metal which oxidizes at low temperatures in dry air, in which it is rapidly coated with a white layer of oxid or hydroxid, and frequently ignites, burning with a violet flame. It must, therefore, be kept under naphtha. It decomposes $H_2O$, or ice, with great energy, the heat of the reaction igniting the liberated H. It combines with Cl with incandescence, and also unites directly with S, P, As, Sb, and Sn. Heated in $CO_2$ it is oxidized, and liberates C.

**Oxids.**—Three are known: $K_2O$; $K_2O_2$; and $K_2O_4$.

**Potassium Hydroxid—Potassium hydrate—Potash—Potassa—***Common caustic*—**Potassa** (U. S.)—**Potassa caustica** (Br.)—KHO—56—is obtained by processes similar to those used in manufacturing NaHO. It is purified by solution in alcohol, evaporation and fusion in a silver basin, and casting in silver moulds—**potash by alcohol**; it is then free from KCl and $K_2SO_4$, but contains small quantities of $K_2CO_3$, and frequently As.

It is usually met with in cylindrical sticks, hard, white, opaque, and brittle. The KHO by alcohol has a bluish tinge, and a smoother surface than the common; sp. gr. 2.1; fuses at dull redness; is freely soluble in $H_2O$, forming a strongly alkaline and caustic liquid; less soluble in alcohol. In air, solid or in solution, it absorbs $H_2O$ and $CO_2$, and is converted into $K_2CO_3$. Its solutions dissolve Cl, Br, I, S, and P. It decomposes the ammoniacal salts, with liberation of $NH_3$; and the salts of many of the metals, with formation of a K salt, and a metallic hydroxid. It dissolves the proteins, and, when heated, decomposes them with formation of leucin, tyrosin, etc. It oxidizes the carbohydrates with formation of potassium oxalate and carbonate. It decomposes the fats with formation of soft soaps.

**Sulfids.**—Five are known: $K_2S$, $K_2S_2$, $K_2S_3$, $K_2S_4$, and $K_2S_5$; also a sulfhydrate: KHS.

**Potassium Monosulfid**—$K_2S$—110—is formed by the action of KHO on KHS. **Potassium Disulfid**—$K_2S_2$—142—is an orange-colored solid, formed by exposing an alcoholic solution of KHS to the air. **Potassium Trisulfid**—$K_2S_3$—174—a brownish yellow mass, obtained by fusing together $K_2CO_3$ and S in the proportion: $4K_2CO_3+10S=SO_4K_2+3K_2S_3+4CO_2$. **Potassium Pentasulfid**—$K_2S_5$—238—is formed, as a brown mass, when $K_2CO_3$ and S are fused together in the proportion: $4K_2CO_3+16\,S=4CO_2+3K_2S_5+K_2SO_4$. **Liver of Sulfur**—*hepar sulfuris*—**potassii sulfuratum** (U. S.; Br.)—is a mixture of $K_2S_3$ and $K_2S_5$.

**Potassium Sulfhydrate**—KHS—72—is formed by saturating a solution of KHO with $H_2S$.

**Potassium Chlorid**—*Sal digestivum Sylvii*—KCl—74.5—exists in nature, either pure or mixed with other chlorids; principally as **carnallite**, KCl, $MgCl_2+6$ Aq. It crystallizes in anhydrous, permanent cubes, soluble in $H_2O$.

**Potassium Bromid**—**Potassii bromidum** (U. S.; Br.)—KBr—119—is formed either by decomposing $FeBr_2$ by $K_2CO_3$, or by dissolving Br in solution of KHO. In the latter case the bromate formed is converted into KBr, by calcination. It crystallizes in anhydrous cubes or tables; has a sharp, salty taste; very soluble in $H_2O$, sparingly so in alcohol. It is decomposed by Cl with liberation of Br.

**Potassium Iodid**—**Potassii iodidum** (U. S.; Br.)—KI—166—is obtained by saturating KHO solution with I, evaporating, and calcining the resulting mixture of iodid and iodate with charcoal. It frequently contains iodate and carbonate. It crystallizes in cubes, transparent if pure; permanent in air; anhydrous; soluble in $H_2O$ and in alcohol. It is decomposed by Cl, $HNO_3$ and $HNO_2$, with liberation of I. It combines with other iodids to form double iodids. Its solutions dissolve iodin and many metallic iodids.

**Potassium Nitrate**—**Nitre**—**Saltpeter**—**Potassii nitras** (U. S.); **Potassæ nitras** (Br.)—$KNO_3$—101—occurs in nature, and is produced artificially, as a result of the decomposition of nitrogenized organic substances. It is usually obtained by decomposing native $NaNO_3$ by boiling solution of $K_2CO_3$ or KCl.

It crystallizes in six-sided, rhombic prisms, grooved upon the surface; soluble in $H_2O$, with depression of temperature; more soluble in $H_2O$ containing NaCl; very sparingly soluble in alcohol; fuses at 350° (662° F.) without decomposition; gives off O, and is converted into nitrite below redness; more strongly heated, it is decomposed into N, O, and a mixture of K oxids. It is a valuable oxidant at high temperatures. Heated with charcoal it deflagrates.

Gunpowder is an intimate mixture of $KNO_3$ with S and C, in such proportion that the $KNO_3$ yields all the O required for the combustion of the S and C.

**Potassium Hypochlorite**—KClO—90.5—is formed in solution by imperfect saturation of a cooled solution of KHO with hypochlorous acid. An impure solution is used in bleaching: **Javelle water.**

**Potassium Chlorate—Potassii chloras** (U. S.)—**Potassæ chloras** (Br.)—$KClO_3$—122.5—is prepared: (1) by passing Cl through a solution of KHO; (2) by passing Cl over a mixture of milk of lime and KCl, heated to 60° (140° F.); (3) by electrolysis of KCl. By electrolytic action the KCl is split into its ions: $2KCl=2K+2Cl$; these, by secondary reactions with $H_2O$, produce KClO: $K_2+2H_2O=2KHO+H_2$, and $2KHO+Cl_2=2KClO+H_2$, and at the temperature generated, the KClO yields $KClO_3$: $2KClO+H_2O=KClO_3+KCl+H_2$. It crystallizes in transparent, anhydrous plates, soluble in $H_2O$; sparingly soluble in weak alcohol.

It fuses at 400° (752° F.). If further heated, it is decomposed into KCl and perchlorate, and at a still higher temperature the perchlorate is decomposed into KCl and O: $2KClO_3=KClO_4+KCl+O_2$, and $KClO_4=KCl+2O_2$. It is a valuable source of O, and a more active oxidant than $KNO_3$. When mixed with readily oxidizable substances, C, S, P, sugar, tannin, resins, etc., the mixtures explode when subjected to shock. With strong $H_2SO_4$ it gives off $Cl_2O_4$, an explosive yellow gas. It is decomposed by $HNO_3$ with formation of $KNO_3$, $KClO_4$, and liberation of Cl and O. Heated with HCl it gives off a mixture of Cl and $Cl_2O_4$, the latter acting as an energetic oxidant in solutions in which it is generated.

**Sulfates.—Dipotassic sulfate**—*Potassium sulfate*—**Potassii sulfas** (U. S.)—**Potassæ sulfas** (Br.)—$K_2SO_4$—174—occurs native; in the ash of many plants; and in solution in mineral waters. It crystallizes in right rhombic prisms; hard; permanent in air; salt and bitter in taste; soluble in $H_2O$.

**Monopotassic Sulfate.**—*Hydropotassic sulfate*—*Acid sulfate*—$KHSO_4$—136—is formed as a by-product in the manufacture of $HNO_3$. When heated it loses $H_2O$, and is converted into the **pyrosulfate**, $K_2S_2O_7$, which, at a higher temperature, is decomposed into $K_2SO_4$ and $SO_3$.

**Dipotassic Sulfite**—*Potassic sulfite*—**Potassii sulfis** (U. S.)—$K_2SO_3$—158—is formed by saturating solution of $K_2CO_3$ with $SO_2$, and evaporating over $H_2SO_4$. It crystallizes in oblique rhombohedra; soluble in $H_2O$. Its solution absorbs O from the air, with formation of $K_2SO_4$.

**Potassium Dichromate**—*Bichromate of potash*—Potassii bichromas (U. S.)—**Potassæ bichromas** (Br.)—$K_2Cr_2O_7$—294.8—is

formed by heating a mixture of *chrome iron ore* with $KNO_3$, or $K_2CO_3$ in air; extracting with $H_2O$; neutralizing with dilute $H_2SO_4$; and evaporating. It forms large, reddish-orange colored prismatic crystals; soluble in $H_2O$; fuses below redness, and at a higher temperature is decomposed into O, potassium chromate, and chromic oxid. Heated with HCl, it gives off Cl.

**Potassium Permanganate — Potassii permanganas** (U. S.); **Potassæ permanganas** (Br.)—$K_2Mn_2O_8$—314—is obtained by fusing a mixture of manganese dioxid, KHO, and $KClO_3$, and evaporating the solution to crystallization; $K_2MnO_4$, and KCl are first formed; on boiling with $H_2O$, the manganate is decomposed into $K_2Mn_2O_8$, KHO and $MnO_2$.

It crystallizes in dark prisms, almost black, with greenish reflections, which yield a red powder when broken. Soluble in $H_2O$, communicating to it a red color, even in very dilute solution. It is a most valuable oxidizing agent. With organic matter its solution is turned to green, by the formation of the manganate, or deposits the brown sesquioxid of manganese, according to the nature of the organic substance. In some instances the reaction takes place best in the cold, in others under the influence of heat; in some better in acid solutions, in others in alkaline solutions. Mineral reducing agents act more rapidly. Its oxidizing powers render its solutions valuable as disinfectants.

**Potassium Acetate—Potassii acetas** (U. S.); **Potassæ acetas** (Br.)—$KC_2H_3O_2$—110—exists in the sap of plants; and it is by its calcination that the major part of the carbonate of wood ashes is formed. It is prepared by neutralizing acetic acid with $K_2CO_3$ or $KHCO_3$.

It forms crystalline needles, deliquescent, and very soluble in $H_2O$; less soluble in alcohol. Its solutions are faintly alkaline.

**Carbonates.—Dipotassic Carbonate—Potassic Carbonate — Salt of tartar—Pearl ash—Potassii carbonas** (U. S.); **Potassæ carbonas** (Br.)—$K_2CO_3$—138—exists in mineral waters, and in the animal economy. It is prepared industrially, in an impure form, known as **potash** or **pearlash,** from wood ashes, from the molasses of beet sugar, and from the native Stassfurth chlorid. It is obtained pure by decomposing the monopotassic salt, purified by several recrystallizations, by heat; or by calcining a potassium salt of an organic acid. Thus cream of tartar, mixed with nitre and heated to redness, yields a black mixture of C and $K_2CO_3$, called **black flux**; on extracting which with $H_2O$, a pure carbonate, known as **salt of tartar,** is dissolved.

Anhydrous, it is a white, granular, deliquescent, very soluble powder. At low temperatures it crystallizes with 2Aq. Its solution is alkaline.

**Monopotassic Carbonate**—*Hydropotassic carbonate*—**Bicarbonate**—**Potassii bicarbonas** (U. S.); **Potassæ bicarbonas** (Br.)—$HKCO_3$—100—is obtained by dissolving $K_2CO_3$ in $H_2O$, and saturating the solution with $CO_2$. It crystallizes in oblique rhombic prisms, much less soluble than the carbonate. In solution, it is gradually converted into the dipotassic salt when heated, when brought into a vacuum, or when treated with an inert gas. The solutions are alkaline in reaction and in taste, but are not caustic.

The substance used in baking, under the name **salæratus**, is this or the corresponding Na salt, usually the latter. Its extensive use in some parts of the country is undoubtedly in great measure the cause of the prevalence of dyspepsia. When used alone in baking, it "raises" the bread by decomposition into carbon dioxid and dipotassic (or disodic) carbonate, the latter producing disturbances of digestion by its strong alkaline reaction.

**Monopotassic Oxalate**—*Hydropotassic oxalate*—*Binoxalate of potash*—$KHC_2O_4$—128—forms transparent, soluble, acid needles. It occurs along with the **quadroxalate** $HKC_2O_4$, $H_2C_2O_4+2Aq$, in **salt of lemon** or **salt of sorrel**, used in straw bleaching, and for the removal of ink-stains, etc. It closely resembles Epsom salt in appearance, and has been fatally mistaken for it.

**Tartrates.**—**Dipotassic Tartrate**—*Potassic tartrate*—**Soluble tartar**—*Neutral tartrate of potash*—**Potassii tartras** (U. S.)—**Potassæ tartras** (Br.)—$K_2C_4H_4O_6$—226—is prepared by neutralizing the hydropotassic salt with potassium carbonate. It forms a white, crystalline powder, very soluble in $H_2O$, the solution being dextrogyrous, $[a]_D=+28.48°$; soluble in alcohol. Acids, even acetic, decompose its solution, with precipitation of the monopotassic salt.

**Monopotassic Tartrate**—*Hydropotassic tartrate*—**Cream of tartar**—**Potassii bitartras** (U. S.)—**Potassæ bitartras** (Br.)—$HKC_4H_4O_6$—188.—During the fermentation of grape juice, as the proportion of alcohol increases, crystalline crusts collect in the cask. These constitute the **crude tartar**, or **argol**, of commerce, which is composed, in great part, of monopotassic tartrate, with some calcium tartrate and coloring matter. The crude product is purified by repeated crystallization from boiling $H_2O$, decolorizing with animal charcoal, digesting the purified tartar with HCl at 20° (68° F.), washing with cold $H_2O$, and crystallizing from hot $H_2O$.

It crystallizes in hard, opaque (translucent when pure), rhombic prisms, which have an acidulous taste, and are very sparingly soluble in $H_2O$, still less soluble in alcohol. Its solution is acid, and dissolves many metallic oxids with formation of double tartrates. When boiled with antimony trioxid, it forms tartar emetic.

It is used in the household, combined with monosodic carbonate,

in baking, the two substances reacting upon each other to form Rochelle salt, with liberation of carbon dioxid.

**Baking Powders** are now largely used as substitutes for yeast to "raise" biscuits, cakes, etc. Their action is based upon the decomposition of $HNaCO_3$ by some salt having an acid reaction, or by a weak acid. In addition to the bicarbonate and flour, or cornstarch (added to render the bulk convenient to handle and to diminish the rapidity of the reaction), they contain cream of tartar, tartaric acid, alum, or acid phosphates. Sometimes ammonium sesquicarbonate is used, in whole or in part, in place of sodium carbonate.

The reactions by which the $CO_2$ is liberated are:

1. $HKC_4H_4O_6$ (Monopotassic tartrate.) + $NaHCO_3$ (Monosodic carbonate.) = $NaKC_4H_4O_6$ (Sodium potassium tartrate.) + $H_2O$ (Water.) + $CO_2$ (Carbon dioxid.)

2. $H_2C_4H_4O_6$ (Tartaric acid.) + $2NaHCO_3$ (Monosodic carbonate.) = $Na_2C_4H_4O_6$ (Disodic tartrate.) + $2H_2O$ (Water.) + $2CO_2$ (Carbon dioxid.)

3. $Al_2(SO_4)_3,K_2SO_4$ (Aluminium potassium alum.) + $6NaHCO_3$ (Monosodic carbonate.) = $K_2SO_4$ (Dipotassic sulfate.) + $3Na_2SO_4$ (Disodic sulfate.) + $Al_2H_6O_6$ (Aluminium hydroxid.) + $6CO_2$ (Carbon dioxid.)

4. $Al_2(SO_4)_3,(NH_4)_2SO_4$ (Aluminium ammonium alum.) + $6NaHCO_3$ (Monosodic carbonate.) = $(NH_4)_2SO_4$ (Diammonic sulfate.) + $3Na_2SO_4$ (Disodic sulfate.) + $Al_2H_6O_6$ (Aluminium hydroxid.) + $6CO_2$ (Carbon dioxid.)

5. $Al_2(SO_4)_3$ (Aluminium sulfate.) + $6NaHCO_3$ (Monosodic carbonate.) = $3Na_2SO_4$ (Disodic sulfate.) + $Al_2H_6O_6$ (Aluminium hydroxid.) + $6CO_2$ (Carbon dioxid.)

6. $NaH_2PO_4$ (Monosodic phosphate.) + $NaHCO_3$ (Monosodic carbonate.) = $Na_2HPO_4$ (Disodic phosphate.) + $H_2O$ (Water.) + $CO_2$ (Carbon dioxid.)

**Sodium Potassium Tartrate—Rochelle salt**—*Sel de seignette*—**Potassii et sodii tartras** (U. S.)—**Soda tartarata** (Br.)—$NaKC_4H_4O_6+4Aq$—210+72—is prepared by saturating monopotassic tartrate with disodic carbonate. It crystallizes in large, transparent prisms, which effloresce superficially in dry air and attract moisture in damp air. It fuses at 70°–80° (158–176° F.), and loses 3Aq at 100° (212° F.). It is soluble in 1.4 parts of cold $H_2O$.

**Potassium Antimonyl Tartrate**—*Tartarated antimony*—**Tartar emetic—Antimonii et potassii tartras** (U. S.)—**Antimonium tartaratum** (Br.)—$(SbO)KC_4H_4O_6+\frac{1}{2}Aq$—331.6—is prepared by boil-

ing a mixture of 3 pts. $Sb_2O_3$ and 4 pts. $HKC_4H_4O_6$ in $H_2O$ for an hour, filtering, and allowing to crystallize. When required pure, it must be made from pure materials.

It crystallizes in transparent, soluble, right rhombic octahedra, which turn white in air. Its solutions are acid in reaction, have a nauseating metallic taste, and are precipitated by alcohol. The crystals contain ½ Aq, which they lose entirely at 100° (212° F.), and, partially, by exposure to air. It is decomposed by the alkalies, alkaline earths, and alkaline carbonates, with precipitation of $Sb_2O_3$. The precipitate is redissolved by excess of soda or potash, or by tartaric acid. HCl, $H_2SO_4$ and $HNO_3$ precipitate corresponding antimonyl compounds from solutions of tartar emetic. It converts mercuric into mercurous chlorid. It forms double tartrates with the tartrates of the alkaloids.

**Potassium Cyanid—Potassii cyanidum** (U. S.)—KCN—65—is obtained by heating a mixture of potassium ferrocyanid and dry $K_2CO_3$, as long as effervescence continues; decanting and crystallizing.

It is usually met with in dull, white, amorphous masses. Odorless when dry, it has the odor of hydrocyanic acid when moist. It is deliquescent, and very soluble in $H_2O$; almost insoluble in alcohol. Its solution is acrid and bitter in taste, with an after-taste of hydrocyanic acid. It is very readily oxidized to the cyanate, a property which renders it valuable as a reducing agent. Solutions of KCN dissolve I, AgCl, the cyanids of Ag and Au, and many metallic oxids.

It is actively poisonous, and produces its effects by decomposition and liberation of hydrocyanic acid (*q. v.*).

**Potassium Ferrocyanid—Yellow prussiate of potash—Potassii ferrocyanidum** (U. S.); **Potassæ prussias flava** (Br.)—$K_4[Fe(CN)_6] + 3$ Aq—367.9+54.—This salt, the source of the other cyanogen compounds, is manufactured by adding nitrogenous organic matter (blood, bones, hoofs, leather, etc.) and iron to $K_2CO_3$ in fusion; or by other processes in which the N is obtained from the residues of the purification of coal gas, from atmospheric air, or from ammoniacal compounds.

It forms soft, flexible, lemon-yellow crystals, permanent in air at ordinary temperatures. They begin to lose Aq at 60° (140° F.), and become anhydrous at 100° (212° F.). Soluble in $H_2O$; insoluble in alcohol, which precipitates it from its aqueous solution. When calcined with KHO or $K_2CO_3$ potassium cyanid and cyanate are formed, and Fe is precipitated. Heated with dilute $H_2SO_4$, it yields an insoluble white or blue salt, potassium sulfate, and hydrocyanic acid. Its solutions form, with those of many of the metallic salts, insoluble ferrocyanids; those of Zn, Pb, and Ag are white, cupric ferrocyanid

is mahogany-colored, ferrous ferrocyanid is bluish white, ferric ferrocyanid, **Prussian blue**, is dark blue. Blue ink is a solution of Prussian blue in a solution of oxalic acid.

**Potassium Ferricyanid—Red prussiate of potash**—$K_6Fe_2(CN)_{12}$—657.8—is prepared by acting upon the ferrocyanid with chlorin; or, better, by heating the white residue of the action of $H_2SO_4$ upon potassium ferrocyanid, in the preparation of hydrocyanic acid, with a mixture of 1 vol. $HNO_3$ and 20 vols. $H_2O$; the *blue* product is digested with $H_2O$, and potassium ferrocyanid, the solution filtered and evaporated. It forms red, oblique rhombic prisms, almost insoluble in alcohol. With solutions of ferrous salts it gives a dark blue precipitate, **Turnbull's blue.**

**Analytical Characters.**—(1) Platinic chlorid, in presence of HCl: yellow ppt., $K_2PtCl_6$; crystalline if slowly formed; sparingly soluble in $H_2O$, much less so in alcohol. (2) Tartaric acid in not too dilute solution: white ppt.; soluble in alkalies and in concentrated acids. (3) Hydrofluosilicic acid: translucent, gelatinous ppt.; forms slowly; soluble in strong alkalies. (4) Perchloric acid: white ppt.; sparingly soluble in $H_2O$; insoluble in alcohol. (5) Phosphomolybdic acid: white ppt.; forms slowly. (6) Colors the Bunsen flame violet (the color is only observable through blue glass in the presence of Na), and exhibits a spectrum of two bright lines: $\lambda = 7860$ and 4045 (Fig. 14, No. 3, p. 22).

**Action of the Sodium and Potassium Compounds on the Economy.**—The hydroxids of Na and K, and in a less degree the carbonates, disintegrate animal tissues, dead or living, with which they come in contact, and, by virtue of this action, act as powerful caustics upon a living tissue. Upon the skin, they produce a soapy feeling, and in the mouth a soapy taste. Like the acids, they cause death, either immediately, by corrosion or perforation of the stomach; or, secondarily, after weeks or months, by closure of one or both openings of the stomach, due to thickening, consequent upon inflammation.

The treatment consists in the neutralization of the alkali by an acid, dilute vinegar. Neutral oils and milk are of service, more by reason of their emollient action than for any power they have to neutralize the alkali, by the formation of a soap, at the temperature of the body.

The other compounds of Na, if the acid be not poisonous, are without deleterious action, unless taken in excessive quantity. Common salt has produced paralysis and death in a dose of half a pound. The neutral salts of K, on the contrary, are by no means without true poisonous action when taken internally, or injected subcutaneously, in sufficient quantities; causing dyspnœa, convulsions, arrest of the

heart's action, and death. In the adult human subject, death has followed the ingestion of doses of 15–30 gms. of the nitrate, in several instances; doses of 8–60 gms. of the sulfate have also proved fatal.

**Cesium**—*Symbol*=Cs—*Atomic weight*=133; and **Rubidium**—*Symbol*=Rb—*Atomic weight*=85.4—are two rare elements, discovered in 1860 by Kirchoff and Bunsen while examining spectroscopically the ash of a spring water. They exist in very small quantity in *lepidolite*. They combine with O and decompose $H_2O$ even more energetically than does K, forming strongly alkaline hydroxids.

## SILVER.

*Symbol*=Ag(*Argentum*)—*Atomic weight*=108 (O=16:107.93; H=1:107.07)—*Molecular weight*=216 (?)—*Sp. gr.*=10.4–10.54—*Fuses at* 1,000° (1,832° F.).

Although silver is usually classed with the "noble metals," it differs from Au and Pt widely in its chemical characters, in which it more closely resembles the alkaline metals.

When pure Ag is required, coin silver is dissolved in $HNO_3$ and the diluted solution precipitated with HCl. The silver chlorid is washed, until the washings no longer precipitate with silver nitrate; and reduced, either (1) by suspending it in dilute $H_2SO_4$ in a platinum basin, with a bar of pure Zn, and washing thoroughly, after complete reduction; or (2) by mixing it with chalk and charcoal (AgCl, 100 parts; C, 5 parts; $CaCO_3$, 70 parts), and gradually introducing the mixture into a red-hot crucible.

Silver is a white metal; very malleable and ductile; the best known conductor of heat and electricity. It is not acted on by pure air, but is blackened in air containing a trace of $H_2S$. It combines directly with Cl, Br, I, S, P, and As. Hot $H_2SO_4$ dissolves it as sulfate, and $HNO_3$ as nitrate. The caustic alkalies do not affect it. It alloys readily with many metals; its alloy with Cu is harder than the pure metal.

Silver seems to exist in a number of allotropic modifications, besides that in which it is ordinarily met with. In one of these it is brilliant, metallic, bluish green in color, and dissolves in $H_2O$, forming a deep red solution; in another it has the color of burnished gold, when dry; and in still another it has also a bluish green color, but is insoluble in water. Very dilute mineral acids immediately convert these modifications into normal gray silver, without evolution of any gas.

**Oxids.**—Three oxids of silver are known: $Ag_4O$, $Ag_2O$, and $Ag_2O_2$.

**Silver Monoxid**—*Protoxid*—**Argenti oxidum**—(U. S.; Br.)—$Ag_2O$—231.8—formed by precipitating a solution of silver nitrate with potash. It is a brownish powder; faintly alkaline and very slightly soluble in $H_2O$; strongly basic. It readily gives up its oxygen. On contact with ammonium hydroxid it forms a fulminating powder.

**Silver Chlorid**—AgCl—143.4—formed when HCl or a chlorid is added to a solution containing silver. It is white; turns violet and black in sunlight; volatilizes at 260° (500° F.); sparingly soluble in HCl; soluble in solutions of the alkaline chlorids, thiosulfates, and cyanids, and in ammonium hydroxid. It crystallizes in octahedra on exposure of its ammoniacal solution.

**Silver Bromid**—AgBr—and **Iodid**—AgI—are yellowish precipitates, formed by decomposing silver nitrate with potassium bromid and iodid. The former is very sparingly soluble in ammonium hydroxid, the latter is insoluble.

**Silver Nitrate**—**Argenti Nitras** (U. S.; Br.)—$AgNO_3$—169.9—is prepared by dissolving Ag in $HNO_3$, evaporating, fusing, and recrystallizing. It crystallizes in anhydrous, right rhombic plates; soluble in $H_2O$. The solutions are colorless and neutral. In the presence of organic matter it turns black in sunlight.

The salt, fused and cast into cylindrical moulds, constitutes **lunar caustic, lapis infernalis; argenti nitras fusa** (U. S.). If, during fusion, the temperature be raised too high, it is converted into nitrite, O, and Ag; and if sufficiently heated leaves pure Ag.

Dry Cl and I decompose it, with liberation of anhydrous $HNO_3$. It absorbs $NH_3$, to form a white solid, $AgNO_3$, $3NH_3$, which gives up its $NH_3$ when heated. Its solution is decomposed very slowly by H, with deposition of Ag.

**Silver Cyanid**—**Argenti Cyanidum**—(U. S.)—AgCN—133.9—is prepared by adding KCN or HCN to a solution of $AgNO_3$. It is a white, tasteless powder; gradually turns brown in daylight; insoluble in dilute acids; soluble in ammonium hydroxid, and in solutions of ammoniacal salts, cyanids, or thiosulfates. The strong mineral acids decompose it with liberation of HCN.

**Analytical Characters.**—(1) Hydrochloric acid: white flocculent ppt.; soluble in $NH_4HO$; insoluble in $HNO_3$. (2) Potash or soda: brown ppt.; insoluble in excess; soluble in $NH_4HO$. (3) Ammonium hydroxid, from neutral solutions: brown ppt.; soluble in excess. (4) Hydrogen sulfid or ammonium sulfhydrate: black ppt.; insoluble in $NH_4HS$. (5) Potassium bromid: yellowish white ppt.; insoluble in acids, if not in great excess; soluble in $NH_4HO$. (6) Potassium iodid; same as KBr, but the ppt. is less soluble in $NH_4HO$.

**Action on the Economy.**—Silver nitrate acts both locally as a

corrosive, and systemically as a true poison. Its local action is due to its decomposition, by contact with organic substances, resulting in the separation of elementary Ag, whose deposition causes a black stain, and liberation of free $HNO_3$, which acts as a caustic. When absorbed, it causes nervous symptoms, referable to its poisonous action. The blue coloration of the skin, observed in those to whom it is administered for some time, is due to the reduction of the metal, under the combined influence of light and organic matter; especially of the latter, as the darkening is observed, although it is less intense, in internal organs.

In acute poisoning by silver nitrate, sodium chlorid or white of egg should be given; and, if the case be seen before the symptoms of corrosion are far advanced, emetics.

## AMMONIUM COMPOUNDS.

**The Ammonium Theory.**—Although the radical **ammonium**, $NH_4$, has probably never been isolated, its existence in the ammoniacal compounds is almost universally admitted. The ammonium hypothesis is based chiefly upon the following facts: (1) the close resemblance of the ammoniacal salts to those of K and Na; (2) when ammonia gas and an acid gas come together, they unite, *without liberation of hydrogen*, to form an ammoniacal salt; (3) the diatomic anhydrids unite directly with dry ammonia with formation of the ammonium salt of an amido acid:

$$\underset{\text{Sulfur trioxid.}}{SO_3} + \underset{\text{Ammonia.}}{2NH_3} = \underset{\text{Ammonium sulfamate.}}{SO_3(NH_2)(NH_4)}$$

(4) when solutions of the ammoniacal salts are subjected to electrolysis, a mixture, having the composition $NH_3+H$ is given off at the negative pole; (5) amalgam of sodium, in contact with a concentrated solution of ammonium chlorid, increases much in volume, and is converted into a light, soft mass, having the luster of mercury. This **ammonium amalgam** is decomposed gradually, giving off ammonia and hydrogen in the proportion $NH_3+H$; (6) if the gases $NH_3+H$, given off by decomposition of the amalgam, exist there in simple solution, the liberated H would have the ordinary properties of that element. If, on the other hand, they exist in combination, the H would exhibit the more energetic affinities of an element in the nascent state. The hydrogen so liberated is in the nascent state.

**Ammonium Hydroxid**—*Caustic ammonia*—$NH_4HO$—35—has never been isolated, probably owing to its tendency to decomposition; $NH_4HO=NH_3+H_2O$. It is considered as existing in the so-called aqueous solutions of ammonia. These are colorless liquids; of less

sp. gr. than $H_2O$; strongly alkaline; and having the taste and odor of ammonia, which gas they give off on exposure to air, and more rapidly when heated. They are neutralized by acids, with elevation of temperature and formation of ammoniacal salts. The **Aqua ammoniæ** (U. S.) and **Liq. ammoniæ** (Br.) are such solutions.

**Sulfids.**—Four are known: $(NH_4)_2S$, $(NH_4)_2S_2$, $(NH_4)_2S_4$, and $(NH_4)_2S_5$; as well as a sulfhydrate $(NH_4)HS$.

**Ammonium Sulfhydrate**—$NH_4HS$—51—is formed, in solution, by saturating a solution of $NH_4HO$ with $H_2S$; or, anhydrous, by mixing equal volumes of dry $NH_3$ and dry $H_2S$.

The anhydrous compound is a colorless, transparent, volatile and soluble solid. The solution, when freshly prepared, is colorless, but soon becomes yellow from oxidation, and formation of ammonium disulfid and thiosulfate, and finally deposits sulfur.

The sulfids and hydrosulfid of ammonium are also formed during the decomposition of protein bodies, and exist in the gases formed in burial vaults, sewers, etc.

**Ammonium Chlorid—Sal ammoniac—Ammonii chloridum** (U. S.; Br.)—$NH_4Cl$—53.5—is obtained from the ammoniacal water of gas works. It is a translucid, fibrous, elastic solid; salty in taste, neutral in reaction; volatile without fusion or decomposition; soluble in $H_2O$. Its solution is neutral, but loses $NH_3$ and becomes acid when boiled.

Ammonium chlorid exists in small quantity in the gastric juice of the sheep and dog; also in the perspiration, urine, saliva and tears.

**Ammonium Bromid—Ammonii bromidum** (U. S.)—$(NH_4)Br$—98—is formed either by combining $NH_3$ and HBr; by decomposing ferrous bromid with $NH_4HO$; or by double decomposition between KBr and $(NH_4)_2SO_4$. It is a white, granular powder, or crystallizes in large prisms, which turn yellow on exposure to air; quite soluble in $H_2O$; volatile without decomposition.

**Ammonium Iodid—Ammonii iodidum** (U. S.)—$NH_4I$—145—is formed by union of equal volumes of $NH_3$ and HI; or by double decomposition of KI and $(NH_4)_2SO_4$. It crystallizes in deliquescent, very soluble cubes.

**Ammonium Nitrate—Ammonii nitras**—(U. S.)—$(NH_4)NO_3$—80—is prepared by neutralizing $HNO_3$ with ammonium hydroxid or carbonate. It crystallizes in flexible, anhydrous, six-sided prisms; very soluble in $H_2O$, with considerable diminution of temperature; fuses at 150° (302° F.), and decomposes at 210° (410° F.), with formation of nitrous oxid: $(NH_4)NO_3=N_2O+2H_2O$. If the heat be suddenly applied, or allowed to surpass 250° (482° F.), $NH_3$, NO, and $N_2O$ are formed. When fused it is an active oxidant.

**Sulfates.**—**Diammonic Sulfate**—*Ammonic sulfate*—**Ammonii**

**sulfas** (U. S.)—$(NH_4)_2SO_4$—132—is obtained by collecting the distillate from a mixture of ammoniacal gas liquor and lime in $H_2SO_4$. It forms anhydrous, soluble, rhombic crystals; fuses at 140° (284° F.), and is decomposed at 200° (392° F.) into $NH_3$ and $H(NH_4)SO_4$.

**Monoammonic Sulfate**—*Hydroammonic sulfate—Bisulfate of ammonia*—$H(NH_4)SO_4$—115—is formed by the action of $H_2SO_4$ on $(NH_4)_2SO_4$. It crystallizes in right rhombic prisms, soluble in $H_2O$ and in alcohol.

**Ammonium Acetate**—$(NH_4)C_2H_3O_2$—77—is formed by saturating acetic acid with $NH_3$, or with ammonium carbonate. It is a white, odorless, very soluble solid; fuses at 86° (186.8° F.), and gives off $NH_3$; then acetic acid, and finally acetamid. **Liq. ammonii acetatis** = **Spirit of Mindererus** is an aqueous solution of this salt.

**Carbonates.—Diammonic Carbonate**—*Ammonic carbonate—Neutral ammonium carbonate*—$(NH_4)_2CO_3+Aq$—96+18—has been obtained as a white crystalline solid. In air it is rapidly decomposed into $NH_3$ and $H(NH_4)CO_3$.

**Monoammonic Carbonate**—*Hydroammonic carbonate—Acid carbonate of ammonia*—$H(NH_4)CO_3$—79—is prepared by saturating a solution of $NH_4HO$ or ammonium sesquicarbonate with $CO_2$. It crystallizes in large, rhombic prisms; quite soluble in $H_2O$. At 60° (140° F.) it is decomposed into $NH_3$ and $CO_2$.

**Ammonium Sesquicarbonate**—**Sal volatile**—**Preston salts**—**Ammonii carbonas** (U. S.); **Ammoniæ carbonas** (Br.)—$NH_4HCO_3+NH_4CO_2NH_2$—157—is prepared by heating a mixture of $NH_4Cl$ or $(NH_4)_2SO_4$ and chalk, and condensing the product. It crystallizes in rhombic prisms; has an ammoniacal odor and an alkaline reaction; soluble in $H_2O$. By exposure to air or by heating its solution, it is decomposed into $H_2O$, $NH_3$, and $H(NH_4)CO_3$. It is not a pure salt, but a mixture of monoammonic carbonate and ammonium carbamate.

**Analytical Characters.**—(1) Entirely volatile at high temperatures. (2) Heated with KHO, the ammoniacal compounds give off $NH_3$, recognizable: (*a*) by changing moist red litmus to blue; (*b*) by its odor; (*c*) by forming a white cloud on contact with a glass rod moistened with HCl. (3) With platinic chlorid: a yellow, crystalline ppt. (4) With hydrosodic tartrate, in moderately concentrated and neutral solution: a white crystalline ppt.

**Action on the Economy.**—Solutions of the hydroxid and carbonate act upon animal tissues in the same way as the corresponding Na and K compounds. They, moreover, disengage $NH_3$, which causes intense dyspnœa, irritation of the air-passages, and suffocation.

The treatment indicated is the neutralization of the alkali by a dilute acid. Usually the vapor of acetic acid or of dilute HCl must be administered by inhalation.

## II. THALLIUM GROUP.

### THALLIUM.

*Symbol*=Tl—*Atomic weight*=204 (O=16:204.1; H=1:202.48)—*Sp. gr.*=11.8–11.9—*Fuses at* 294° (561° F.)—*Discovered by Crookes* (1861).

A rare element, first obtained from the deposits in flues of sulfuric acid factories, in which pyrites from the Hartz were used. It resembles Pb in appearance and in physical properties, but differs entirely from that element in its chemical characters. It resembles Au in being univalent and trivalent, but differs from it, and resembles the alkali metals in being readily oxidized, in forming alums, and in forming no acid hydrate. It differs from the alkali metals in the thallic compounds, which contain $Tl'''$. It is characterized spectroscopically by a bright green line—$\lambda$=5349.

## III. CALCIUM GROUP.

*Metals of the Alkaline Earths.*

CALCIUM—STRONTIUM—BARIUM.

The members of this group are bivalent in all their compounds; each forms two oxids: MO and $MO_2$; each forms a hydroxid, having well-marked basic characters.

### CALCIUM.

*Symbol*=Ca—*Atomic weight*=40 (O=16:40; H=1:39.68)—*Molecular weight*=80 (?)—*Sp. gr.*=1.984—*Discovered by Davy in* 1808—*Name from* calx=lime.

Occurs only in combination, as limestone, marble, chalk ($CaCO_3$), gypsum, selenite, alabaster ($CaSO_4$), and many other minerals. In bones, egg-shells, oyster-shells, etc., as $Ca_3(PO_4)_2$ and $CaCO_3$, and in many vegetable structures.

The element is obtained by electrolysis of fused $CaCl_2$, or by heating $CaI_2$ with Na. It is a hard, yellow, very ductile, and malleable metal; fusible at a red heat; not sensibly volatile. In dry air it is not altered, but is converted into $CaH_2O_2$ in damp air; decomposes $H_2O$; burns when heated in air.

**Calcium Monoxid—Quick Lime—Lime—Calx** (U. S.; Br.)—CaO—56—is prepared by heating a native carbonate (limestone); or,

when required pure, by heating a carbonate, prepared by precipitation.

It occurs in white or grayish, amorphous masses; odorless; alkaline, caustic; almost infusible; sp. gr. 2.3. With $H_2O$ it gives off great heat and is converted into the hydroxid (**slaking**). In air it becomes **air-slaked**, falling into a white powder, having the composition $CaCO_3$, $CaH_2O_2$.

**Calcium Hydroxid—Slaked lime—Calcis hydras** (Br.)—$CaH_2O_2$—74—is formed by the action of $H_2O$ on CaO. If the quantity of $H_2O$ used be one-third that of the oxid, the hydroxid remains as a dry, white, odorless powder; alkaline in taste and reaction; more soluble in cold than in hot $H_2O$. If the quantity of $H_2O$ be greater, a creamy or milky liquid remains, **cream, or milk of lime**; a solution holding an excess in suspension. With a sufficient quantity of $H_2O$ the hydroxid is dissolved to a clear solution, which is **lime water—Liquor calcis** (U. S.; Br.). The solubility of $CaH_2O_2$ is diminished by the presence of alkalies, and is increased by sugar or mannite; **Liq. calc. saccharatus** (Br.); **Syrupus calcis** (U. S.). Solutions of $CaH_2O_2$ absorb $CO_2$ with formation of a white deposit of $CaCO_3$.

**Calcium Carbide**—$CaC_2$—is formed by the action of a very high temperature upon a mixture of quick lime and carbon. It is an amorphous grayish substance, which is decomposed by water, yielding acetylene gas: $CaC_2+2H_2O=C_2H_2+Ca(OH)_2$. One kilo. $CaC_2$ yields 440 litres $C_2H_2$.

**Calcium Chlorid—Calcii chloridum** (U. S.; Br.)—$CaCl_2$—111—is obtained by dissolving marble in HCl: $CaCO_3+2HCl=CaCl_2+H_2O+CO_2$. It is bitter, deliquescent, very soluble in $H_2O$; crystallizes with 6Aq, which it loses when fused, leaving a white, amorphous mass, used as a drying agent.

**Chloride of Lime—Bleaching powder—Calx chlorata** (U. S.; Br.)—is a white or yellowish, hygroscopic powder, prepared by passing Cl over $CaH_2O_2$, maintained in excess. It is bitter and acrid in taste; soluble in cold $H_2O$; decomposed by boiling $H_2O$, and by the weakest acids, with liberation of Cl. It is decomposed by $CO_2$, with formation of $CaCO_3$, and liberation of hypochlorous acid, if it be moist; or of Cl, if it be dry. A valuable disinfectant. The "available chlorin" is the amount liberated by acids, and should exceed 35%.

Bleaching powder was formerly considered as a mixture of calcium chlorid and hypochlorite, formed by the reaction: $2CaO+2Cl_2=CaCl_2+Ca(ClO)_2$, but it is more probable that it is a definite compound having the formula $CaCl(OCl)$, which is decomposed by $H_2O$ into a mixture of $CaCl_2$ and $Ca(ClO)_2$; and by dilute $HNO_3$ or $H_2SO_4$ with formation of HClO.

**Calcium Sulfate**—$CaSO_4$—136—occurs in nature as *anhydrite;* and with 2Aq in **gypsum,** *alabaster, selenite;* and in solution in natural waters. **Terra alba** is ground gypsum. It crystallizes with 2Aq in right rhombic prisms; sparingly soluble in $H_2O$, more soluble in $H_2O$ containing free acids or chlorids. When the hydrated salt (gypsum) is heated to 80° (176° F.), or, more rapidly, between 120°–130° (248°–266° F.), it loses its Aq and is converted into a white, opaque mass, which, when ground, is **plaster of Paris.**

The **setting** of plaster when mixed with $H_2O$, is due to the conversion of the anhydrous into the crystalline, hydrated salt. The ordinary plastering should never be used in hospitals, as, by reason of its irregularities and porosity, it soon becomes saturated with septic germs, and cannot be thoroughly purified by disinfectants. Plaster surfaces may, however, be rendered dense, and be highly polished, so as to be smooth and impermeable, by adding glue and alum, or an alkaline silicate to the water used in mixing.

**Phosphates.**—Three are known: $Ca_3(PO_4)_2$; $Ca_2(HPO_4)_2$, and $Ca(H_2PO_4)_2$.

**Tricalcic Phosphate**—*Tribasic* or *neutral phosphate*—**Bone phosphate**—**Calcii phosphas præcipitatus** (U. S.)—**Calcis phosphas** (Br.)—$Ca_3(PO_4)_2$—310—occurs in nature, in soils, guano, *coprolites,* phosphorite, in all plants, and in every animal tissue and fluid. It is obtained by dissolving bone-ash in HCl, filtering, and precipitating with $NH_4HO$; or by double decomposition between $CaCl_2$ and an alkaline phosphate. When freshly precipitated it is gelatinous; when dry, a light, white, amorphous powder; almost insoluble in pure $H_2O$; soluble to a slight extent in $H_2O$ containing ammoniacal salts, or NaCl or $NaNO_3$; readily soluble in dilute acids, even in $H_2O$ charged with carbonic acid. It is decomposed by $H_2SO_4$ into $CaSO_4$ and $Ca(H_2PO_4)_2$. **Bone-ash** is an impure form of $Ca_3(PO_4)_2$, obtained by calcining bones, and used in the manufacture of P and of superphosphate.

**Dicalcic Phosphate**—$Ca_2(HPO_4)_2+2Aq$—272+36—is a crystalline, insoluble salt; formed by double decomposition between $CaCl_2$ and $HNa_2PO_4$ in acid solution.

**Monocalcic Phosphate**—*Acid calcium phosphate*—**Superphosphate of lime**—$Ca(H_2PO_4)_2$—234—exists in brain tissue, and in those animal liquids whose reaction is acid. It is also formed when $Ca_3(PO_4)_2$ is dissolved in an acid, and is manufactured for use as a manure, by decomposing bone-ash with $H_2SO_4$. It crystallizes in pearly plates; very soluble in $H_2O$. Its solutions are acid.

**Calcium Carbonate**—$CaCO_3$—100—the most abundant of the natural compounds of Ca, exists as *limestone, calcspar, chalk, marble, Iceland spar,* and *arragonite;* and forms the basis of corals, shells of

crustacea and of molluscs, etc. **Otoliths**, which occur in the internal ear, parotid calculi, and sometimes vesical calculi consist of $CaCO_3$.

**Precipitated chalk—Calcii carbonas præcipitata** (U. S.; Br.)—is prepared by precipitating a solution of $CaCl_2$ with one of $Na_2CO_3$. **Prepared chalk—Creta præparata** (U. S.; Br.)—is native chalk, purified by grinding with $H_2O$, diluting, allowing the coarser particles to subside, decanting the still turbid liquid, collecting and drying the finer particles. A process known as **elutriation** or **levigation.**

It is a white powder, almost insoluble in pure $H_2O$; much more soluble in $H_2O$ containing carbonic acid, the solution being regarded as containing **monocalcic carbonate** $H_2Ca(CO_3)_2$. At a red heat it yields $CO_2$ and CaO. It is decomposed by acids with liberation of $CO_2$.

**Calcium Oxalate**—*Oxalate of lime*—$CaC_2O_4$—128—exists in the sap of many plants, in human urine, and in **mulberry calculi**, and is formed as a white, crystalline precipitate, by double decomposition, between a Ca salt and an alkaline oxalate. It is insoluble in $H_2O$, acetic acid, or $NH_4HO$; soluble in the mineral acids and in solution of $H_2NaPO_4$.

**Analytical Characters.**—(1) Ammonium sulfhydrate: nothing, unless the Ca salt be the phosphate, oxalate or fluorid, when it forms a white ppt. (2) Alkaline carbonates: white ppt.; not prevented by the presence of ammoniacal salts. (3) Ammonium oxalate: white ppt., insoluble in acetic acid; soluble in HCl or $HNO_3$. (4) Sulfuric acid: white ppt., either immediately or on dilution with three volumes of alcohol; very sparingly soluble in $H_2O$, insoluble in alcohol; soluble in sodium thiosulfate solution. (5) Sodium tungstate: dense white ppt., even from dilute solutions. (6) Colors the flame of the Bunsen burner reddish-yellow, and exhibits a spectrum of a number of bright bands, the most prominent of which are: $\lambda$=6265, 6202, 6181, 6044, 5982, 5933, 5543, and 5517.

## STRONTIUM.

*Symbol*=Sr—*Atomic weight*=87.5 (O=16:86.9; H=1:87.6)—*Sp. gr.*=2.54.

An element, not as abundant as Ba, occurring principally in the minerals *strontianite* ($SrCO_3$) and *celestine* ($SrSO_4$). Its compounds resemble those of Ca and Ba. Its nitrate is used in making red fire. The **iodid** and the **lactate** are used in medicine.

**Analytical Characters.**—(1) Behaves like Ba with alkaline carbonates and $Na_2HPO_4$. (2) Calcium sulfate: a white ppt., which forms slowly; accelerated by addition of alcohol. (3) The Sr com-

pounds color the Bunsen flame red, or, as observed through blue glass, purple or rose color. The Sr flame gives a spectrum of many bands, of which the most prominent are: λ=6694, 6664, 6059, 6031, 4607.

## BARIUM.

*Symbol*=Ba—*Atomic weight*=137.5 (O=16:137.4; H=1: 136.3)—*Molecular weight*=273.6 (†)—*Sp. gr.*=4.0—Discovered by Davy, 1808—Name from βαρὺς=heavy.

Occurs only in combination, principally as *heavy spar* ($BaSO_4$) and *witherite* ($BaCO_3$). It is a pale yellow, malleable metal, quickly oxidized in air, and decomposing $H_2O$ at ordinary temperatures.

**Oxids.—Barium Monoxid—Baryta**—BaO—153.4—is prepared by calcining the nitrate. It is a grayish-white or white, amorphous, caustic solid. In air it absorbs moisture and $CO_2$, and combines with $H_2O$ as does CaO.

**Barium Dioxid**—*Barium peroxid*—$BaO_2$—169.4—is prepared by heating the monoxid in O. It is a grayish-white, amorphous solid. Heated in air it is decomposed: $BaO_2=BaO+O$. Aqueous acids dissolve it with formation of a barytic salt and $H_2O_2$.

**Barium Hydroxid**—$BaH_2O_2$—171.5—is prepared by the action of $H_2O$ on BaO. It is a white, amorphous solid, soluble in $H_2O$. Its aqueous solution, **baryta water**, is alkaline, and absorbs $CO_2$, with formation of a white deposit of $BaCO_3$.

**Barium Chlorid**—$BaCl_2+2$ Aq—208.3+36—is obtained by treating BaS or $BaCO_3$ with HCl. It crystallizes in prismatic plates, permanent in air, soluble in $H_2O$.

**Barium Nitrate**—$Ba(NO_3)_2$—261.4—is prepared by neutralizing $HNO_3$ with $BaCO_3$. It forms octahedral crystals, soluble in $H_2O$.

**Barium Sulfate**—$BaSO_4$—233.4—occurs in nature as *heavy spar*, and is formed as an amorphous, white powder, insoluble in acids, by double decomposition between a Ba salt and a sulfate in solution. It is insoluble in $H_2O$ and in acids. It is used as a pigment, **permanent white.**

**Barium Carbonate**—$BaCO_3$—197.4—occurs in nature as *witherite*, and is formed by double decomposition between a Ba salt and a carbonate in alkaline solution. It is a heavy, amorphous, white powder, insoluble in $H_2O$, soluble with effervescence in acids.

**Analytical Characters.**—(1) Alkaline carbonates: white ppt., in alkaline solution. (2) Sulfuric acid, or calcium sulfate: white ppt., insoluble in acids. (3) Sodium phosphate: white ppt., soluble in $HNO_3$. (4) Colors the Bunsen flame greenish-yellow, and exhibits a spectrum of several lines, the most prominent of which are: λ=6108, 6044, 5881, 5536.

**Action on the Economy.**—The oxids and hydroxid act as corrosives, by virtue of their alkalinity, and also as true poisons. All soluble compounds of Ba, and those which are readily converted into soluble compounds in the stomach, are actively poisonous. Soluble sulfids, followed by emetics, are indicated as antidotes. The sulfate, notwithstanding its insolubility in water, is poisonous to some animals.

## IV. MAGNESIUM GROUP.

### MAGNESIUM—ZINC—CADMIUM.

Each of these elements forms a single oxid—a corresponding basic hydroxid, and a series of salts in which its atoms are bivalent.

The existence of potassium zincate, $ZnO_2K_2$, obtainable by the action of zinc hydroxid and potassium hydroxid upon each other: $Zn(OH)_2+2KHO=ZnO_2K_2+2H_2O$ would seem to require the transferral of zinc to the amphoteric class; the $Zn(OH)_2$ in the above reaction fulfilling the requirements of the second definition of acids (see p. 42). Potassium zincate should, however, be considered rather as a double oxid of zinc and potassium: $ZnOK_2O$ or Zn.OK.OK, than as a true salt for the following reasons: (1) It is also produced by the reaction: $Zn+2KHO=ZnO_2K_2+H_2$, in which, if $ZnO_2K_2$ be a salt, KHO, the most distinctly basic substance known, must be considered to be an acid. (2) In the electrolysis of $ZnO_2K_2$ the Zn and K go to the negative pole, and the O to the positive, while in the electrolysis of true ternary salts, such as $K_2SO_4$, the oxygen accompanies the other electro-negative element to the positive pole, the metal going alone to the negative. Moreover, the zincates are unstable bodies, and the most prominent function of $Zn(OH)_2$ is that of a base, as in the reaction $Zn(OH)_2+H_2SO_4=ZnSO_4+2HO_2$. (See Aluminium, p. 198).

### MAGNESIUM.

*Symbol*=Mg—*Atomic weight*=24 (O = 16:24.36; H = 1:24.17)—*Molecular weight*=48 (?)—*Sp. gr.*=1.75—Fuses at 1000° (1832° F.)—*Discovered by Davy*, 1808.

Occurs as carbonate in *dolomite* or *magnesian limestone*, and as silicate in *mica*, *asbestos*, *soapstone*, *meerschaum*, *talc*, and in other minerals. It also accompanies Ca in the forms in which it is found in the animal and vegetable worlds.

It is prepared by heating its chlorid with Na, or by electrolysis of the fused chlorid. It is a hard, light, malleable, ductile, white metal. It burns with great brilliancy when heated in air (magnesium light),

but may be distilled in H. The flash light used by photographers is a mixture of powdered Mg with an oxidizing agent, $KClO_3$ or $KNO_3$. It decomposes vapor of $H_2O$ when heated; reduces $CO_2$ with the aid of heat, and combines directly with Cl, S, P, As and N. It dissolves in dilute acids, but is not affected by alkaline solutions.

**Magnesium Oxid—Calcined magnesia—Magnesia** (U. S.; Br.) —MgO—40—is obtained by calcining the carbonates, hydroxid, or nitrate. It is a light, bulky, tasteless, odorless, amorphous, white powder; alkaline in reaction; almost insoluble in $H_2O$; readily soluble without effervescence in acids.

**Magnesium Hydroxid**—$MgH_2O_2$—58—occurs in nature, and is formed when a solution of a Mg salt is precipitated with excess of NaHO, in absence of ammoniacal salts. It is a heavy, white powder, insoluble in $H_2O$; absorbs $CO_2$.

**Magnesium Chlorid**—$MgCl_2$—95—is formed when MgO or $MgCO_3$ is dissolved in HCl. It is an exceedingly deliquescent, soluble substance, which is decomposed into HCl and MgO when its aqueous solutions are evaporated to dryness. Like all the soluble Mg compounds it is bitter in taste, and accompanies the sulfate and bicarbonate in the *bitter waters*.

**Magnesium Sulfate—Epsom salt**—*Seidlitz salt*—**Magnesii sulfas** (U. S.)—**Magnesiæ sulfas** (Br.)—$MgSO_4+7Aq$—120+126—exists in solution in sea water and in the waters of many mineral springs, especially those known as **bitter waters**. It is formed by the action of $H_2SO_4$ on $MgCO_3$. It crystallizes in right rhombic prisms; bitter; slightly effervescent, and quite soluble in $H_2O$. Heated, it fuses and gradually loses 6Aq up to 132° (269.6° F.); the last Aq it loses at 210° (410° F.).

**Phosphates.**—Resemble those of Ca in their constitution and properties, and accompany them in the situations in which they occur in the animal body, but in much smaller quantity.

Magnesium also forms double phosphates, constituted by the substitution of one atom of the bivalent metal for two of the atoms of basic hydrogen, of a molecule of phosphoric acid, and of an atom of alkaline metal, or of an ammonium group, for the remaining basic hydrogen.

**Ammonio-Magnesian Phosphate—Triple phosphate**—$Mg(NH_4)PO_4+6Aq$—137+108—is produced when an alkaline phosphate and $NH_4HO$ are added to a solution containing Mg. When heated it is converted into **magnesium pyrophosphate**, $Mg_2P_2O_7$, in which form $H_3PO_4$ and Mg are usually weighed in quantitative analysis.

**Carbonates.—Magnesium Carbonate**—*Neutral carbonate*—$MgCO_3$ —84—exists native in *magnesite*, and, combined with $CaCO_3$, in *dolomite*. It cannot be formed, like other carbonates, by decomposing

a Mg salt with an alkaline carbonate, but may be obtained by passing $CO_2$ through $H_2O$ holding tetramagnesic tricarbonate in suspension.

**Trimagnesic Dicarbonate**—$(MgCO_3)_2MgH_2O_2+2Aq$—226+36—is formed, in small crystals, when a solution of $MgSO_4$ is precipitated with excess of $Na_2CO_3$, and the mixture boiled.

**Tetramagnesic Tricarbonate—Magnesia alba—Magnesii carbonas** (U. S.)—**Magnesiæ carbonas** (Br.)—$(MgCO_3)_3MgH_2O_2+3Aq$—310+54—occurs in commerce in light, white cubes, composed of a powder which is amorphous, or partly crystalline. It is prepared by precipitating a solution of $MgSO_4$ with one of $Na_2CO_3$. If the precipitation occur in cold, dilute solutions (Magnesiæ carbonas lœvis, Br.), very little $CO_2$ is given off; a light, bulky precipitate falls, and the solution contains magnesium, probably in the form of the bicarbonate $Mg(HCO_3)_2$. This solution, on standing, deposits crystals of the carbonate, $MgCO_3+3Aq$. If hot concentrated solutions be used, and the liquid be then boiled upon the precipitate, $CO_2$ is given off, and a denser, heavier precipitate is formed, which varies in composition, according to the length of time during which the boiling is continued, and to the presence or absence of excess of sodium carbonate. The pharmaceutical product frequently contains $(MgCO_3)_4$, $MgH_2O_2+4H_2O$, or even $(MgCO_3)_2,MgH_2O_2+2H_2O$. All of these compounds are very sparingly soluble in $H_2O$, but much more soluble in $H_2O$ containing ammoniacal salts.

**Analytical Characters.**—(1) Ammonium hydroxid: voluminous, white ppt. from neutral solutions. (2) Potash or soda: voluminous, white ppt. from warm solutions, prevented by the presence of $NH_4$ salts, and of certain organic substances. (3) Ammonium carbonate: slight ppt. from hot solutions; prevented by the presence of $NH_4$ salts. (4) Sodium or potassium carbonate: white ppt., best from hot solution; prevented by the presence of $NH_4$ compounds. (5) Disodic phosphate: white ppt. in hot, not too dilute solutions. (6) Oxalic acid: nothing alone, but in presence of $NH_4HO$, a white ppt.; not formed in presence of salts of $NH_4$.

## ZINC.

*Symbol*=Zn—*Atomic weight* = 65 (O =16:65.4; H =1:64.88)—*Molecular weight*=65—*Sp. gr.*=6.862-7.215—*Fuses at* 415° (779° F.)—*Distils at* 1040° (1904° F.).

Occurs principally in *calamine* ($ZnCO_3$); and *blende* (ZnS); also as oxid and silicate; never free. It is separated from its ores by calcining, roasting, and distillation.

It is a bluish-white metal; crystalline, granular, or fibrous; quite malleable and ductile when pure. The commercial metal is usually

brittle. At 130°–150° (266°–302° F.) it is pliable, and becomes brittle again above 200°–210° (392°–410° F.).

At 500° (932° F.) it burns in air, with a greenish-white flame, and gives off snowy-white flakes of the oxid (*lana philosophica; nil album; pompholix*). In moist air it becomes coated with a film of hydrocarbonate. It decomposes steam when heated.

Pure $H_2SO_4$ and pure Zn do not react together in the cold. If the acid be diluted, however, it dissolves the Zn, with evolution of H, and formation of $ZnSO_4$, in the presence of a trace of Pt or Cu. The commercial metal dissolves readily in dilute $H_2SO_4$, with evolution of H, and formation of $ZnSO_4$, the action being accelerated in presence of Pt, Cu, or As. Zinc surfaces, thoroughly coated with a layer of an amalgam of Hg and Zn, are only attacked by $H_2SO_4$ if they form part of closed galvanic circuit; hence the zincs of galvanic batteries are protected by *amalgamation*. Zinc also decomposes $HNO_3$, HCl, and acetic acid. Zinc dissolves in strong solutions of the caustic alkalies with evolution of hydrogen and formation of double oxids (zincates): $Zn+2KHO=ZnO_2K_2+H_2$. It also decomposes many metallic salts in solution with deposition of the metal.

When required for toxicological analysis, zinc must be perfectly free from As, and sometimes from P. It is better to test samples until a pure one is found, than to attempt the purification of a contaminated metal.

Zinc surfaces are readily attacked by weak organic acids. Vessels of *galvanized iron* or *sheet zinc* should therefore never be used to contain articles of food or medicines.

**Zinc Oxid—Zinci oxidum** (U. S.; Br.)—ZnO—81.4—is prepared either by calcining the precipitated carbonate, or by burning Zn in a current of air. An impure oxid, known as **tutty**, is deposited in the flues of zinc furnaces, and in those in which brass is fused. When obtained by calcination of the carbonate, it forms a soft, white, tasteless, and odorless powder. When produced by burning the metal, it occurs in light, voluminous, white masses. It is neither fusible, volatile, nor decomposable by heat, and is completely insoluble in neutral solvents. It dissolves in dilute acids, with formation of the corresponding salts.

It is used in the arts of a white pigment in place of lead carbonate, and is not darkened by $H_2S$.

**Zinc Hydroxid**—$ZnH_2O_2$—99.4—is not formed by union of ZnO and $H_2O$; but is produced when a solution of a Zn salt is treated with KHO. Freshly prepared, it is very soluble in alkalies, and in solutions of $NH_4$ salts.

**Zinc Chlorid—Butter of zinc—Zinci chloridum** (U. S.; Br.)—$ZnCl_2+Aq$—136.3+18—is obtained by dissolving Zn in HCl, or by

heating Zn in Cl. It is a soft, white, very deliquescent, fusible, volatile mass; very soluble in $H_2O$, somewhat less so in alcohol. Its solution has a burning, metallic taste; destroys vegetable tissues; dissolves silk; and exerts a strong dehydrating action upon organic substances in general.

In dilute solution it is used as a disinfectant and antiseptic (*Burnett's fluid*), as a preservative of wood and as an embalming injection.

**Zinc Sulfate—White vitriol—Zinci sulfas** (U.S.; Br.)—$ZnSO_4 + n$Aq—161.4+*n*18—is formed when Zn, ZnO, ZnS, or $ZnCO_3$ is dissolved in diluted $H_2SO_4$. It crystallizes below 30° (86° F.) with 7 Aq; at 30° (86° F.) with 6 Aq; between 40°–50° (104°–122° F.) with 5 Aq; at 0° (32° F.) from concentrated acid solution with 4 Aq. From a boiling solution it is precipitated by concentrated $H_2SO_4$ with 2 Aq; from a saturated solution at 100° (212° F.) with 1 Aq; and anhydrous, when the salt with 1 Aq is heated to 238° (460° F.).

The salt usually met with is that with 7 Aq, which is in large, colorless, four-sided prisms; efflorescent; very soluble in $H_2O$, sparingly soluble in weak alcohol. Its solutions have a strong, styptic taste: coagulate albumen when added in moderate quantity, the coagulum dissolving in an excess; and form insoluble precipitates with the tannins.

**Carbonates.—Zinc Carbonate**—$ZnCO_3$—125.4—occurs in nature as *calamine*. If an alkaline carbonate be added to a solution of a Zn salt, the neutral carbonate, as in the case of Mg, is not formed, but an oxycarbonate, $n ZnCO_3$, $n ZnH_2O_2$ [Zinci carbonas (U. S.; Br.)], whose composition varies with the conditions under which it is formed.

**Analytical Characters.**—(1) K, Na or $NH_4$ hydroxid: white ppt., soluble in excess. (2) Carbonate of K or Na: white ppt., in absence of $NH_4$ salts. (3) Hydrogen sulfid, in neutral solution: white ppt. In presence of an excess of a mineral acid, the formation of this ppt. is prevented, unless sodium acetate be also present. (4) Ammonium sulfhydrate: white ppt., insoluble in excess, in KHO, $NH_4HO$, or acetic acid; soluble in dilute mineral acids. (5) Ammonium carbonate: white ppt., soluble in excess. (6) Disodic phosphate, in absence of $NH_4$ salts: white ppt., soluble in acids or alkalies. (7) Potassium ferrocyanid: white ppt., insoluble in HCl.

**Action on the Economy.**—All the compounds of Zn which are soluble in the digestive fluids behave as true poisons; and solutions of the chlorid (in common use by tinsmiths, and in disinfecting fluids) have also well-marked corrosive properties. When Zn compounds are taken, it is almost invariably by mistake for other substances: the sulfate for Epsom salt, and solutions of the chlorid for various liquids, such as gin, fluid magnesia, vinegar, etc.

Metallic zinc is dissolved by solutions containing NaCl, or organic

acids, for which reason articles of food kept in vessels of galvanized iron become contaminated with zinc compounds, and, if eaten, produce more or less intense symptoms of intoxication. For the same reason materials intended for analysis in cases of supposed poisoning, *should never be packed in jars closed by zinc caps.*

### CADMIUM.

*Symbol*=Cd—*Atomic weight*=111.5 (O=16:112.4; H=1:111.5)—*Molecular weight*=111.8—*Sp. gr.*=8.604—*Fuses at* 227.8° (442° F.)—*Boils at* 860° (1580° F.).

A white metal, malleable and ductile at low temperature, brittle when heated; which accompanies Zn in certain of its ores. It resembles zinc in its physical as well as its chemical characters. It is used in certain fusible alloys, and its iodid is used in photography.

**Analytical Characters.**—Hydrogen sulfid: bright yellow ppt.; insoluble in $NH_4HS$, and in dilute acids and alkalies, soluble in boiling $HNO_3$ or HCl.

## V. ALUMINIUM GROUP.

BERYLLIUM—ALUMINIUM—SCANDIUM—GALLIUM—INDIUM.

These elements form one series of compounds, corresponding to the ferric, containing the group $(M_2)^{vi}$, but no compounds corresponding to the ferrous M″ and the Ni and Co salts are known. Indeed, certain organic compounds, such as aluminium acetylacetonate, $Al(C_5H_7O_2)_3$, seem to contain single, trivalent atoms of the metal. The existence of the aluminates, such as $K_2Al_2O_4$, would seem to place aluminium in the amphoteric class. These compounds, which are formed by the reactions: $Al_2(OH)_6+2KHO=K_2Al_2O_4+4H_2O$, and $Al_2+2KHO+2H_2O=K_2Al_2O_4+3H_2$, are double oxids rather than salts. They resemble the zincates and what has been said concerning those compounds (see p. 193) applies also to the aluminates.

### ALUMINIUM.

*Symbol*=Al—*Atomic weight*=27 (O=16:27.1; H=1:26.88)—*Molecular weight*=55 (?)—*Sp. gr.*=2.56–2.67—*Fuses at about* 700° (1292° F.)—*Name from* alumen=*alum*—*Discovered by Wöhler*, 1827.

Occurrence.—Exceedingly abundant in the clays as *silicate*. Also in *feldspar*, *mica*, and *garnet*, *topaz*, and *emerald*. As a fluorid in *cryolite*, and as a hydroxid in *beauxite*.

**Preparation.**—(1) By decomposing vapor of aluminium chlorid by Na or K (Wöhler). (2) Aluminium hydroxid, mixed with sodium chlorid and charcoal, is heated in Cl, by which a double chlorid of Na and Al ($Na_2Al_2Cl_8$) is formed. This is then heated with Na, when Al and NaCl are produced. (3) These "chemical methods" have been replaced, in the industrial preparation of aluminium, by the electrolytic method, in which a mixture of cryolite and beauxite is treated in an electric furnace.

**Properties.**—*Physical.*—A bluish-white metal; hard; quite malleable, and ductile, when annealed from time to time; slightly magnetic; a good conductor of electricity; non-volatile; very light, and exceedingly sonorous.

*Chemical.*—It is not affected by air or O, except at very high temperatures, and then only superficially. If, however, it contain Si, it burns readily in air, forming aluminium silicate. It does not decompose $H_2O$ at a red heat; but in contact with Cu, Pt, or I, it does so at 100° (212° F.). It combines directly with B, Si, Cl, Br, and I. It is attacked by HCl, gaseous or in solution, with evolution of H, and formation of $Al_2Cl_6$. It dissolves in alkaline solutions, with formation of **aluminates**, and liberation of H. It alloys with Cu to form a golden yellow metal (**aluminium bronze**).

**Aluminium Oxid**—*Alumina*—$Al_2O_3$—102.2—occurs in nature, nearly pure, as *corundum*, *emery*, *ruby*, *sapphire*, and *topaz;* and is formed artificially, by calcining the hydrate, or ammonia alum, at a red heat.

It is a light, white, odorless, tasteless powder; fuses with difficulty; and, on cooling, solidifies in very hard crystals. Unless it has been heated to bright redness, it combines with $H_2O$, with elevation of temperature. It is almost insoluble in acids and alkalies. $H_2SO_4$, diluted with an equal bulk of $H_2O$, dissolves it slowly as $(Al_2)(SO_4)_3$. Fused potash and soda combine with it to form aluminates. It is not reduced by charcoal.

**Aluminium Hydroxid**—*Aluminium hydrate*—**Aluminii hydras** (U. S.)—$Al_2H_6O_6$—156.2—is formed when a solution of aluminium salt is decomposed by an alkali, or alkaline carbonate. It constitutes a gelatinous mass, which, when dried, leaves an amorphous, translucid mass; and, when pulverized, a white, tasteless, amorphous powder. When the liquid in which it is formed contains coloring matters, these are carried down with it, and the dried deposits are used as pigments, called **lakes.**

When freshly precipitated, it is insoluble in $H_2O$; soluble in acids, and in solutions of the fixed alkalies. When dried at a temperature above 50° (122° F.), or after 24 hours' contact with the mother liquor, its solubility is greatly diminished. With acids it

forms salts of aluminium; and with alkalies, aluminates of the alkaline metal. Heated to near redness, it is decomposed into $Al_2O_3$, and $H_2O$. A soluble modification is obtained by dialyzing a solution of $Al_2H_6O_6$ in $Al_2Cl_6$, or by heating a dilute solution of aluminium acetate for 24 hours.

**Aluminates** are for the most part crystalline, soluble compounds, obtained by the action of metallic oxids or hydroxids upon alumina. **Potassium aluminate**, $K_2Al_2O_4 + 3Aq$, is formed by dissolving recently precipitated aluminium hydroxid in potash solution. It forms white crystals, very soluble in $H_2O$, insoluble in alcohol; caustic and alkaline. By a large quantity of $H_2O$ it is decomposed into aluminium hydroxid and a more alkaline salt, $K_6Al_4O_9$.

**Sodium Aluminate.**—The aluminate $Na_6Al_2O_6$ is formed when cryolite is heated with calcium carbonate (see sodium carbonate). Another salt, having the composition $Na_6Al_4O_9$, is prepared by heating to redness a mixture of 1 pt. sodium carbonate and 2 pts. of a native ferruginous aluminium hydrate (beauxite). Both salts are soluble in $H_2O$, and are decomposed by carbonic acid, with precipitation of aluminium hydroxid.

**Aluminium Chlorid**—$Al_2Cl_6$—266.9—is prepared by passing Cl over a mixture of $Al_2O_3$ and C, heated to redness, or by heating clay in a mixture of gaseous HCl and vapor of $CS_2$.

It crystallizes in colorless, hexagonal prisms; fusible; volatile; deliquescent; very soluble in $H_2O$ and in alcohol. From a hot, concentrated solution, it separates in prisms with 12Aq. At very high temperatures $Al_2Cl_6$ appears to be dissociated into $2AlCl_3$.

The disinfectant called **chloralum** is a solution of impure $Al_2Cl_6$.

**Aluminium Sulfate—Aluminii sulfas** (U. S.)—$(Al_2)(SO_4)_3 + 18Aq$—342.2+324—is obtained by dissolving $Al_2H_6O_6$ in $H_2SO_4$; or (industrially) by heating clay with $H_2SO_4$.

It crystallizes, with difficulty, in thin, flexible plates; soluble in $H_2O$; very sparingly soluble in alcohol. Heated, it fuses in its Aq, which it gradually loses up to 200° (392° F.), when a white, amorphous powder, $(Al_2)(SO_4)_3$, remains: this is decomposed at a red heat, leaving a residue of pure alumina.

**Alums**—are double sulfates of the alkaline metals, and the higher sulfates of this, or the iron group. When crystallized, they have the general formula: $(M_2)^{vi}(SO_4)_3$, $R'_2SO_4 + 24Aq$, in which (M) may be $(Fe_2)$, $(Mn_2)$, $(Cr_2)$, $(Al_2)$, or $(Ga_2)$; and $R_2$ may be $K_2$, $Na_2$, $Rb_2$, $Cs_2$, $Tl_2$, or $(NH_4)_2$. They are isomorphous with each other.

**Alumen** (U. S.)—$Al_2(SO_4)_3$, $K_2SO_4 + 24Aq$—516.5+432—is manufactured from "alum shale," and is formed when solutions of the sulfates of Al and K are mixed in suitable proportion.

It crystallizes in large, transparent, regular octahedra; has a sweetish, astringent taste, and is readily soluble in $H_2O$. Heated, it fuses in its Aq at 92° (197.6° F.); and gradually loses 45.5 per cent. of its weight of $H_2O$, as the temperature rises to near redness. The product, known as **burnt alum = alumen exsiccatum** (U. S.), is $(Al)_2(SO_4)_3$, $K_2SO_4$, and is slowly, but completely, soluble in 20–30 pts. $H_2O$. At a bright red heat, $SO_2$ and O are given off, and $Al_2O_3$ and potassium sulfate remain; at a higher temperature, potassium aluminate is formed. Its solutions are acid in reaction; dissolve Zn and Fe with evolution of H; and deposit $Al_2H_6O_6$ when treated with ammonium hydroxid.

**Alumen** (Br.)—$Al_2(SO_4)_3$, $(NH_4)_2SO_4$+24Aq—474.2+432—is the compound now usually met with as **alum**, both in this country and in England. It differs from potash alum in being more soluble in $H_2O$, between 20°–30° (68°–86° F.), and less soluble at other temperatures; and in the action of heat upon it. At 92° (197.6° F.) it fuses in its Aq; at 205° (401° F.), it loses its ammonium sulfate, leaving a white, hygroscopic substance, very slowly and incompletely soluble in $H_2O$. More strongly heated, it leaves alumina. Alum is used in dyeing, and in purification of water by precipitation.

**Silicates**—are very abundant in the different varieties of *clay*, *feldspar*, *albite*, *labradorite*, *mica*, etc. The clays are hydrated aluminium silicates, more or less contaminated with alkaline and earthy salts and iron, to which last certain clays owe their color. The purest is **kaolin**, or porcelain clay, a white or grayish powder. They are largely used in the manufacture of the different varieties of bricks, terra cotta, pottery, and porcelain. *Porcelain* is made from the purer clays, mixed with sand and feldspar; the former to prevent shrinkage, the latter to bring the mixture into partial fusion, and to render the product translucent. The fashioned articles are subjected to a first baking. The porous, baked clay is then coated with a *glaze*, usually composed of oxid of lead, sand and salt. During a second baking the glaze fuses, and coats the article with a hard, impermeable layer. The coarser articles of pottery are glazed by throwing sodium chlorid into the fire; the salt is volatilized, and on contact with the hot aluminium silicate, deposits a coating of the fusible sodium silicate, which hardens on cooling.

**Analytical Characters.**—(1) Potash, or soda: white ppt., soluble in excess. (2) Ammonium hydroxid: white ppt., almost insoluble in excess, especially in presence of ammoniacal salts. (3) Sodium phosphate: white ppt., readily soluble in KHO and NaHO, but not in $NH_4HO$; soluble in mineral acids, but not in acetic acid. (4) Blowpipe—on charcoal does not fuse, and moistened with cobalt nitrate solution turns dark sky-blue.

## BERYLLIUM—SCANDIUM—GALLIUM—INDIUM.

*Symbols and atomic weights*=Be(Gl); 9—Sc; 45—Ga; 70—In; 114.

These elements occur in nature in very small quantities: Beryllium in the emerald and beryl; scandium in gadolinite and euxenite; gallium and indium in certain zinc blendes. Beryllium, also called **Glucinium**, the most abundant of the group, was discovered by Vauquelin, in 1797; the others have been discovered by spectroscopic methods; scandium by Nilson, in 1879; gallium by Boisbaudran, in 1876, and indium by Reich and Richter, in 1863.

The discovery of Sc and Ga affords most flattering verifications of predictions based upon purely theoretical considerations.

It has been observed that there exist numerical relations between the atomic weights of the elements, which, in groups of allied elements differ from each other by (approximately) some multiple of eight. Upon this variation Mendelejeff has based what is known as the **Periodic Law**, to the effect that: "**The properties of elements, the constitution of their compounds and the properties of the latter, are periodic functions of the atomic weights of the elements.**"

In accordance with this law the elements may be thus arranged:

| Series. | Group I. | Group II. | Group III. | Group IV. | Group V. | Group VI. | Group VII. | Group VIII. |
|---|---|---|---|---|---|---|---|---|
| | $R_2O$ | RO | $R_2O_3$ | $RH_4$ $RO_2$ | $RH_3$ $R_2O_5$ | $RH_2$ $RO_3$ | RH $R_2O_7$ | $(R_2H)$ $(RO_4)$ |
| 1 | H=1 | | | | | | | |
| 2 | Li=7 | Be=9 | B=11 | C=12 | N=14 | O=16 | F=19 | |
| 3 | Na=23 | Mg=24 | Al=27 | Si=28 | P=31 | S=32 | Cl=35 | Cu=63 Fe=56 |
| 4 | K=39 | Ca=40 | Sc=44 | Ti=48 | V=51 | Cr=52 | Mn=55 | Co=59 Ni=59 |
| 5 | (Cu=63) | Zn=65 | Ga=69 | Ge=72 | As=75 | Se=78 | Br=80 | Ru=101 |
| 6 | Rb=85 | Sr=87 | Yt=88 | Zr=90 | Nb=94 | Mo=96 | ?=100 | Pd=106 Ag=108 |
| 7 | (Ag=108) | Cd=112 | In=113 | Sn=118 | Sb=120 | Te=125 | I=127 | Rh=139 |
| 8 | Cs=133 | Ba=137 | La=137 | Ce=139 | Nd=143 | Sm=150 | | |
| 9 | | | E=166 | | | | | Os=191 Ir=192 |
| 10 | | | Yb=172 | | Ta=182 | W=184 | ?=190 | Pt=193 Au=196 |
| 11 | (Au=196) | Hg=200 | Tl=204 | Pb=207 | Bi=208 | | | |
| 12 | | | | Th=231 | | U=238 | | |

The atomic weights and chemical characters, which were announced by Mendelejeff in 1870 as those of the undiscovered elements which would occupy the positions 4 and 5 in Group III, have been since found to be those of Sc and Ga. Still later, the vacant positions 10, III, 5, IV, and 8, VI, have been filled by the discovery of Yb, Ge, and Sm.

# VI. NICKEL GROUP.

## NICKEL—COBALT.

These two elements bear some resemblance chemically to those of the Fe group; from which they differ in forming, so far as known, no compounds similar to the ferrates, chromates, and manganates, unless the barium cobaltite, described by Rousseau, be such. They form compounds corresponding to $Fe_2O_3$, but those corresponding to the ferric salts are either wanting or exceedingly unstable.

### NICKEL.

*Symbol*=Ni=*Atomic weight*=58 (O=16:58.7; H=1:58.22)—*Sp. gr.*=8.637.

Occurs in combination with S, and with S and As.

It is a white metal, hard, slightly magnetic, not tarnished in air. *German silver* is an alloy of Ni, Cu, and Zn. Nickel is now extensively used for plating upon other metals, and for the manufacture of dishes, etc., for use in the laboratory. Its salts are green.

**Nickelous Sulfate**—$NiSO_4$—is obtained by dissolving the metal, hydroxid or carbonate in $H_2SO_4$. It forms green crystals with 7 Aq, and combines with $(NH_4)_2SO_4$ to form a double sulfate, used in the nickel-plating bath, for which use it must be free from K or Na.

**Analytical Characters.**—(1) Ammonium sulfhydrate: black ppt.; insoluble in excess. (2) Potash or soda: apple-green ppt., in absence of tartaric acid; insoluble in excess. (3) Ammonium hydroxid: apple-green ppt.; soluble in excess; forming a violet solution, which deposits the apple-green hydrate, when heated with KHO.

### COBALT.

*Symbol*=Co—*Atomic weight*=59 (O=16:59; H=59.53)—*Sp. gr.*=8.5–8.7.

Occurs in combination with As and S. Its salts are red when hydrated, and usually blue when anhydrous. Its phosphate is used as a blue pigment.

**Analytical Characters.**—(1) Ammonium sulfhydrate: black ppt.; insoluble in excess. (2) Potash: blue ppt.; turns red, slowly in the cold, quickly when heated; not formed in the cold in the presence of $NH_4$ salts. (3) Ammonium hydroxid: blue ppt.; turns red in absence of air, green in its presence.

## VII. COPPER GROUP.

### COPPER—MERCURY.

Each of these elements forms two series of compounds. One contains compounds of the bivalent group $\left(\begin{smallmatrix}Cu\\|\\Cu\end{smallmatrix}\right)''$ or $(Hg_2)''$, which are designated by the termination **ous**; the other contains compounds of single, bivalent atoms Cu″ or Hg″, which are designated by the termination **ic.**

### COPPER.

*Symbol*=Cu (*Cuprum*)—*Atomic weight*=63 (O=16:63.6; H=1:63.09)—*Molecular weight*=127 (?)—*Sp. gr.*=8.914–8.952—*Fuses at* 1091° (1996° F.).

**Occurrence.**—It is found free, in crystals or amorphous masses, sometimes of great size; also as sulfid, *copper pyrites;* oxid, *ruby ore* and *black oxid;* and basic carbonate, *malachite.*

**Properties.**—*Physical.*—A yellowish-red metal; dark-brown when finely divided; very malleable, ductile, and tenacious; a good conductor of heat and electricity; has a peculiar, metallic taste and a characteristic odor.

*Chemical.*—It is unaltered in dry air at the ordinary temperature; but, when heated to redness, is oxidized to CuO. In damp air it becomes coated with a brownish film of oxid; a green film of basic carbonate; or, in salt air, a green film of basic chlorid. Hot $H_2SO_4$ dissolves it with formation of $CuSO_4$ and $SO_2$. It is dissolved by $HNO_3$ with formation of $Cu(NO_3)_2$ and NO; and by HCl with liberation of H. Weak acids form with it soluble salts, in presence of air and moisture. It is dissolved by $NH_4HO$, in presence of air, with formation of a blue solution. It combines directly with Cl, frequently with light.

**Oxids.**—**Cuprous Oxid**—*Suboxid or red oxid of copper*—$(Cu_2)O$—143.2—is formed by calcining a mixture of $(Cu_2)Cl_2$ and $Na_2CO_3$; or a mixture of CuO and Cu. It is a red or yellow powder; permanent in air; sp. gr. 5.749–6.093; fuses at a red heat; easily reduced by C or H. Heated in air it is converted into CuO.

**Cupric Oxid**—*Binoxid or black oxid of copper*—CuO—79.6—is prepared by heating Cu to dull redness in air; or by calcining $Cu(NO_3)_2$; or by prolonged boiling of the liquid over a precipitate, produced by heating a solution of a cupric salt, in presence of glucose, with KHO. By the last method it is sometimes produced in Trommer's test for glucose, when an excessive quantity of $CuSO_4$ has been used.

It is a black, or dark reddish-brown, amorphous solid; readily reduced by C, H, Na, or K at comparatively low temperatures. When heated with organic substances, it gives up its O, converting the C into $CO_2$, and the H into $H_2O$: $C_2H_6O+6CuO=6Cu+2CO_2+3H_2O$; a property which renders it valuable in organic analysis, as by heating a known weight of organic substance with CuO, and weighing the amount of $CO_2$ and $H_2O$ produced, the percentage of C and H may be obtained. It dissolves in acids with formation of salts.

**Hydroxids.—Cuprous Hydroxid**—$(Cu)_2H_2O_2(?)$—160.4 (?)—is formed as a yellow or red powder when mixed solutions of $CuSO_4$ and KHO are heated in presence of glucose. By boiling the solution it is rapidly dehydrated with formation of $(Cu_2)O$.

**Cupric Hydroxid**—$CuH_2O_2$—97.6—is formed by the action of KHO upon solution of $CuSO_4$, in absence of reducing agents and in the cold. It is a bluish, amorphous powder; very unstable, and readily dehydrated, with formation of CuO.

**Sulfids.—Cuprous Sulfid**—*Subsulfid or protosulfid of copper*—$Cu_2S$—159.2—occurs in nature as *copper glance* or *chalcosine*, and in many double sulfids, **pyrites**.

**Cupric Sulfid**—CuS—95.6—is formed by the action of $H_2S$, or of $NH_4HS$, on solutions of cupric salts. It is almost black when moist, greenish-brown when dry. Hot $HNO_3$ oxidizes it to $CuSO_4$; hot HCl converts it into $CuCl_2$, with separation of S, and formation of $H_2S$. It is sparingly soluble in $NH_4HS$, its solubility being increased by the presence of organic matter.

**Chlorids.—Cuprous Chlorid**—*Subchlorid or protochlorid*—$(Cu_2)Cl_2$—198.1—is prepared by heating Cu with one of the chlorids of Hg; by dissolving $(Cu_2)O$ in HCl, without contact of air; or by the action of reducing agents on solutions of $CuCl_2$. It is a heavy, white powder; turns violet and blue by exposure to light; soluble in HCl; insoluble in $H_2O$. It forms a crystallizable compound with CO; and its solution in HCl is used in analysis to absorb that gas.

**Cupric Chlorid**—*Chlorid or deutochlorid*—$CuCl_2$—134.5—is formed by dissolving Cu in aqua regia. If the Cu be in excess, it reduces $CuCl_2$ to $(Cu_2)Cl_2$. It crystallizes in bluish-green, rhombic prisms with 2 Aq; deliquescent; very soluble in $H_2O$ and in alcohol.

**Cupric Nitrate**—$Cu(NO_3)_2$—187.6—is formed by dissolving Cu, CuO, or $CuCO_3$ in $HNO_3$. It crystallizes at 20°–25° (68°–77° F.) with 3 Aq; below 20° (68° F.) with 6 Aq, forming blue, deliquescent needles. Strongly heated, it is converted into CuO.

**Cupric Sulfate—Blue vitriol—Blue stone—Cupri sulfas** (U. S.; Br.)—$CuSO_4+5Aq$—159.6+90—is prepared: (1) by roasting CuS; (2) from the water of copper mines; (3) by exposing Cu, moistened with dilute $H_2SO_4$, to air; (4) by heating Cu with $H_2SO_4$.

As ordinarily crystallized, it is in fine, blue, oblique prisms; soluble in $H_2O$; insoluble in alcohol; efflorescent in dry air at 15° (59° F.), losing 2 Aq. At 100° (212° F.) it still retains 1 Aq, which it loses at 230° (446° F.), leaving a white, amorphous powder of the anhydrous salt, which, on taking up $H_2O$, resumes its blue color. Its solutions are blue, acid, styptic, and metallic in taste.

When $NH_4HO$ is added to a solution of $CuSO_4$, a bluish-white precipitate falls, which redissolves in excess of the alkali, to form a deep blue solution. Strong alcohol floated over the surface of this solution separates long, right rhombic prisms, having the composition $CuSO_4,4NH_3+H_2O$, which are very soluble in $H_2O$. This solution constitutes **ammonio-sulfate of copper** or **aqua sapphirina.**

**Cupric Arsenite—Scheele's green — Mineral green** — is a mixture of cupric arsenite, $HCuAsO_3$, and hydroxid; prepared by adding potassium arsenite to solution of $CuSO_4$. It is a grass-green powder, insoluble in $H_2O$; soluble in $NH_4HO$, or in acids. Exceedingly poisonous.

**Schweinfurt Green — Mitis green** or **Paris green** — is the most frequently used, and the most dangerous of the cupro-arsenical pigments. It is prepared by adding a thin paste of neutral cupric acetate with $H_2O$ to a boiling solution of arsenous acid, and continuing the boiling during a further addition of acetic acid. It is an insoluble, green, crystalline powder, having the composition $(C_2H_3O_2)_2Cu+3Cu(AsO_2)_2$, and is therefore cupric aceto-metarsenite. It is decomposed by prolonged boiling in $H_2O$, by aqueous solutions of the alkalies, and by the mineral acids.

**Carbonates.** — The existence of cuprous carbonate is doubtful. **Cupric carbonate**—$CuCO_3$ — exists in nature, but has not been obtained artificially. **Dicupric carbonate** — $CuCO_3,CuH_2O_2$ — exists in nature as **malachite.** When a solution of a cupric salt is decomposed by an alkaline carbonate, a bluish precipitate, having the composition $CuCO_3,CuH_2O_2+H_2O$, is formed, which, on drying, loses $H_2O$, and becomes green; it is used as a pigment under the name **mineral green.** **Tricupric carbonate** —*Sesquicarbonate of copper*— $2(CuCO_3)$, $CuH_2O_2$ — exists in nature as a blue mineral, called **azurite** or **mountain blue,** and is prepared by a secret process for use as a pigment known as **blue ash.**

**Acetates.— Cupric Acetate**—*Diacetate* —*Crystals of Venus* —**Cupri acetas** (U. S.)—$Cu(C_2H_3O_2)_2+Aq$—181.6+18—is formed when CuO or verdigris is dissolved in acetic acid; or by decomposition of a solution of $CuSO_4$ by $Pb(C_2H_3O_2)_2$. It crystallizes in large, bluish-green prisms, which lose their Aq at 140° (284°F.). At 240°–260° (464°–500° F.) they are decomposed with liberation of glacial acetic acid.

**Basic Acetates.**—**Verdigris**—is a substance prepared by exposing to air piles composed of alternate layers of grape-skins and plates of copper, and removing the bluish-green coating from the copper. It is a mixture, in varying proportions, of three different substances: $(C_2H_3O_2)_2Cu_2H_2O_2+5Aq$; $[(C_2H_3O_2)_2Cu]_2,CuH_2O_2+5Aq$; and $(C_2H_3O_2)_2Cu,2(CuH_2O_2)$.

**Analytical Characters.**—CUPROUS—are very unstable and readily converted into cupric compounds. (1) Potash: white ppt.; turning brownish. (2) Ammonium hydroxid, in absence of air: a colorless liquid; turns blue in air.

CUPRIC—are white when anhydrous; when soluble in $H_2O$ they form blue or green, acid solutions. (1) Hydrogen sulfid: black ppt.; insoluble in KHS or NaHS; sparingly soluble in $NH_4HS$; soluble in hot concentrated $HNO_3$ and in KCN. (2) Alkaline sulfhydrates: same as $H_2S$. (3) Potash or soda: pale blue ppt.; insoluble in excess. If the solution be heated over the ppt., the latter contracts and turns black. (4) Ammonium hydroxid, in small quantity: pale blue ppt.; in larger quantity: deep blue solution. (5) Potassium or sodium carbonate: greenish-blue ppt.; insoluble in excess; turning black when the liquid is boiled. (6) Ammonium carbonate: pale blue ppt.; soluble with deep blue color in excess. (7) Potassium cyanid: greenish-yellow ppt.; soluble in excess. (8) Potassium ferrocyanid: chestnut-brown ppt.; insoluble in weak acids; decolorized by KHO. (9) Iron is coated with metallic Cu.

**Action on the Economy.**—The opinion, formerly universal among toxicologists, that all the compounds of copper are poisonous, has been much modified by later researches. Certain of the copper compounds, such as the sulfate, having a tendency to combine with protein and other animal substances, produce symptoms of irritation by their direct local action, when brought in contact with the gastric or intestinal mucous membrane. One of the characteristic symptoms of such irritation is the vomiting of a greenish matter, which develops a blue color upon the addition of $NH_4HO$.

Cases are not wanting in which severe illness, and even death, has followed the use of food which has been in contact with imperfectly tinned copper vessels. Cases in which nervous and other symptoms referable to a truly poisonous action have occurred. As, however, it has also been shown that non-irritant, *pure* copper compounds may be taken in considerable doses with impunity, it appears at least probable that the poisonous action attributed to copper is due to other substances. The tin and solder used in the manufacture of copper utensils contain lead, and in some cases of so-called copper-poisoning, the symptoms have been such as are as consistent with lead-poisoning as with copper-poisoning. Copper is also notoriously

liable to contamination with arsenic, and it is by no means improbable that compounds of that element are the active poisonous agents in some cases of supposed copper-intoxication. Nor is it improbable that articles of food allowed to remain exposed to air in copper vessels should undergo those peculiar changes which result in the formation of poisonous substances, such as the sausage- or cheese-poisons, or the ptomaïns.

The treatment, when irritant copper compounds have been taken, should consist in the administration of white of egg or of milk, with whose proteins an inert compound is formed by the copper salt. If vomiting do not occur spontaneously, it should be induced by the usual methods.

The detection of copper in the viscera after death is not without interest, especially if arsenic have been found, in which case its discovery or non-discovery enables us to differentiate between poisoning by the arsenical greens, and that by other arsenical compounds. The detection of mere traces of copper is of no significance, because, although copper is not a physiological constituent of the body, it is almost invariably present, having been taken with the food.

Pickles and canned vegetables are sometimes intentionally *greened* by the addition of copper; this fraud is readily detected by inserting a large needle into the pickle or other vegetable; if copper be present the steel will be found to be coated with copper after half an hour's contact.

## MERCURY.

*Symbol*=Hg (*Hydrargyrum*)—*Atomic weight*=200 (O=16:200.3; H=1:198.7)—*Molecular weight*=198.7—*Sp. gr. of liquid*=13.596; *of vapor*=6.97—*Fuses at* —38.8° (—37.9° F.)—*Boils at* 358° (676.4° F.).

**Occurrence.**—Chiefly as *cinnabar* (HgS); also in small quantity free and as chlorid.

**Preparation.**—The commercial product is usually obtained by simple distillation in a current of air: $HgS+O_2=Hg+SO_2$. If required pure, it must be freed from other metals by distillation, and agitation of the redistilled product with mercurous nitrate solution, solution of $Fe_2Cl_6$, or dilute $HNO_3$.

**Properties.**—*Physical.*—A bright metallic liquid; volatile at all temperatures. Crystallizes in octahedra of sp. gr. 14.0. When pure, it rolls over a smooth surface in round drops. The formation of tear-shaped drops indicates the presence of impurities.

*Chemical.*—If pure, it is not altered by air at the ordinary temperature, but, if contaminated with foreign metals, its surface becomes dimmed. Heated in air, it is oxidized superficially to HgO. It

does not decompose $H_2O$. It combines directly with Cl, Br, I, and S. It alloys readily with most metals to form **amalgams.** It amalgamates with Fe and Pt only with difficulty. Hot, concentrated, $H_2SO_4$ dissolves it, with evolution of $SO_2$, and formation of $HgSO_4$. It dissolves in cold $HNO_3$, with formation of a nitrate.

Elementary mercury is insoluble in $H_2O$, and probably in the digestive liquids. It enters, however, into the formation of three medicinal agents: **hydrargyrum cum creta** (U. S.; Br.); **massa hydrargyri** (U. S.)=**pilula hydrargyri** (Br.); and **unguentum hydrargyri** (U. S.; Br.), all of which owe their efficacy, not to the metal itself, but to a certain proportion of oxid, produced during their manufacture. The fact that blue mass is more active than mercury with chalk is due to the greater proportion of oxid contained in the former. It is also probable that absorption of vapor of Hg by cutaneous surfaces is attended by its conversion into $HgCl_2$.

**Oxids.—Mercurous Oxid**—*Protoxid or black oxid of mercury*—$(Hg_2)O$—416.6—is obtained by adding a solution of $(Hg_2)(NO_3)_2$ to an excess of solution of KHO. It is a brownish black, tasteless powder; very prone to decomposition into HgO and Hg. It is converted into $(Hg_2)Cl_2$ by HCl; and by other acids into the corresponding mercurous salts.

It is formed by the action of $CaH_2O_2$ on mercurous compounds, and exists in **black wash.**

**Mercuric Oxid**—*Red, or binoxid of mercury*—**Hydrargyri oxidum flavum** (U. S.; Br.)—**Hydrargyri oxidum rubrum** (U. S.; Br.)—HgO—216.3—is prepared by two methods: (1) by calcining $Hg(NO_3)_2$, as long as brown fumes are given off (*Hydr. oxid. rubr.*): or, (2) by precipitating a solution of a mercuric salt by excess of KHO (*Hydr. oxid. flavum*). The products obtained, although the same in composition, differ in physical characters and in the activity of their chemical actions. That obtained by (1) is red and crystalline; that obtained by (2) is yellow and amorphous. The latter is much the more active in its chemical and medicinal actions.

It is very sparingly soluble in $H_2O$, the solution having an alkaline reaction, and a metallic taste. It exists both in solution and in suspension in **yellow wash,** prepared by the action of $CaH_2O_2$ on a mercuric compound.

Exposed to light and air, it turns black, more rapidly in presence of organic matter, giving off O, and liberating Hg: $HgO = Hg + O$. It decomposes the chlorids of many metallic elements in solution, with formation of a metallic oxid and mercuric oxychlorids. It combines with alkaline chlorids to form soluble double chlorids, called **chloromercurates** or **chlorhydrargyrates**; and forms similar compounds with alkaline iodids and bromids.

**Sulfids.—Mercurous Sulfid**—$(Hg_2)S$—432.6—a very unstable compound, formed by the action of $H_2S$ on mercurous salts.

**Mercuric Sulfid**—*Red sulfid of mercury*—**Cinnabar**—**Vermilion**—**Hydrargyri sulfidum rubrum** (U. S.)—HgS—232.3—exists in nature in amorphous red masses, or in red crystals, and is the chief ore of Hg. If Hg and S be ground up together in the cold, or if a solution of a mercuric salt be completely decomposed by $H_2S$, a black sulfid is obtained, which is the **Æthiops mineralis** of the older pharmacists.

A **red sulfid** is obtained for use as a pigment (**vermilion**), by agitating for some hours at 60° (140° F.) a mixture of Hg, S, KHO, and $H_2O$. It is a fine, red powder, which turns brown, and finally black, when heated. Heated in air, it burns to $SO_2$ and Hg. It is decomposed by strong $H_2SO_4$, but not by $HNO_3$ or HCl.

**Chlorids.—Mercurous Chlorid**—*Protochlorid or mild chlorid of mercury*—**Calomel**—**Hydrargyri chloridum mite** (U. S.)—**Hydrargyri subchloridum** (Br.)—$(Hg_2)Cl_2$—471.5—is now principally obtained by mutual decomposition of NaCl and $(Hg_2)SO_4$. Mercuric sulfate is first obtained by heating together 2 pts. Hg and 3 pts. $H_2SO_4$; the product is then caused to combine with a quantity of Hg equal to that first used, to form $(Hg_2)SO_4$; which is then mixed with dry NaCl, and the mixture heated in glass vessels, connected with condensing chambers; $2NaCl + (Hg_2)SO_4 = Na_2SO_4 + (Hg_2)Cl_2$.

In practice, varying quantities of $HgCl_2$ are also formed, and must be removed from the product by washing with boiled, distilled $H_2O$, until the washings no longer precipitate with $NH_4HO$. The presence of $HgCl_2$ in calomel may be detected by the formation of a black stain upon a bright copper surface, immersed in the calomel, moistened with alcohol; or by the production of a black color by $H_2S$ in $H_2O$ which has been in contact with and filtered from calomel so contaminated.

Calomel is also formed in a number of other reactions: (1) By the action of Cl upon excess of Hg. (2) By the action of Hg upon $Fe_2Cl_6$. (3) By the action of HCl, or of a chlorid, upon $(Hg_2)O$, or upon a mercurous salt. (2) By the action of reducing agents, including Hg, upon $HgCl_2$.

Calomel crystallizes in nature, and, when sublimed, in quadratic prisms. When precipitated it is deposited as a heavy, amorphous, white powder, faintly yellowish, and producing a yellowish mark when rubbed upon a dark surface. It sublimes, without fusing, between 420° and 500° (788°–932° F.), is insoluble in cold $H_2O$ and in alcohol; soluble in boiling $H_2O$ to the extent of 1 part in 12,000. When boiled with $H_2O$ for some time, it suffers partial decomposition, Hg is deposited and $HgCl_2$ dissolves.

Although $Hg_2Cl_2$ is insoluble in $H_2O$, in dilute HCl and in pepsin solution, it is dissolved at the body temperature in an aqueous solution of pepsin acidulated with HCl.

When exposed to light, calomel becomes yellow, then gray, owing to partial decomposition, with liberation of Hg and formation of $HgCl_2$: $(Hg_2)Cl_2=Hg+HgCl_2$. It is converted into $HgCl_2$ by Cl or aqua regia: $(Hg_2)Cl_2+Cl_2=2HgCl_2$. In the presence of $H_2O$, I converts it into a mixture of $HgCl_2$ and $HgI_2$: $(Hg_2)Cl_2+I_2=HgCl_2+HgI_2$. It is also converted into $HgCl_2$ by HCl and by alkaline chlorids: $(Hg_2)Cl_2=HgCl_2+Hg$. This change occurs in the stomach when calomel is taken internally, and that to such an extent when large quantities of NaCl are taken with the food, that calomel cannot be used in naval practice as it may be with patients who do not subsist upon salt provisions. It is converted by KI into $(Hg_2)I_2$: $(Hg_2)Cl_2+2KI=2KCl+(Hg_2)I_2$; which is then decomposed by excess of KI into Hg and $HgI_2$, the latter dissolving: $(Hg_2)I_2=Hg+HgI_2$. Solutions of the sulfates of Na, K and $NH_4$ dissolve notable quantities of $(Hg_2)Cl_2$. The hydroxids and carbonates of K and Na decompose it with formation of $(Hg_2)O$: $(Hg_2)Cl_2+Na_2CO_3=(Hg_2)O+CO_2+2NaCl$; and the $(Hg_2)O$ so formed is decomposed into HgO and Hg. If alkaline chlorids be also present, they react upon the HgO so produced, with formation of $HgCl_2$.

**Mercuric Chlorid**—*Perchlorid or bichlorid of mercury*—**Corrosive sublimate—Hydrargyri chloridum corrosivum** (U. S.); **Hydrargyri perchloridum** (Br.)—$HgCl_2$—271.2—is prepared by heating a mixture of 5 pts. dry $HgSO_4$ with 5 pts. dry NaCl, and 1 pt. $MnO_2$ in a glass vessel communicating with a condensing chamber.

It crystallizes by sublimation in octahedra, and by evaporation of its solutions in flattened, right rhombic prisms; fuses at 265° (509° F.), and boils at about 295° (563° F.); soluble in $H_2O$ and in alcohol; very soluble in hot HCl, the solution gelatinizing on cooling. Its solutions have a disagreeable, acid, styptic taste, and are highly poisonous. Although $HgCl_2$ is heavier than water (sp. gr.=5.4) when the crystalline powder is thrown upon water a portion floats for some time.

It is easily reduced to $(Hg_2)Cl_2$ and Hg, and its aqueous solutions are so decomposed when exposed to light; a change which is retarded by the presence of NaCl. Heated with Hg, it is converted into $(Hg_2)Cl_2$. When dry $HgCl_2$, or its solution, is heated with Zn, Cd, Ni, Fe, Pb, Cu, or Bi, those elements remove part or all of its Cl, with separation of $(Hg_2)Cl_2$ or Hg. Its solution is decomposed by $H_2S$, with separation of a yellow sulfochlorid, which, with an excess of the gas, is converted into black HgS. It is soluble without decomposition in $H_2SO_4$, $HNO_3$, and HCl. It is decomposed by KHO or

NaHO, with separation of a brown oxychlorid if the alkaline hydroxid be in limited quantity; or of the orange-colored HgO if it be in excess. A similar decomposition is effected by $CaH_2O_2$ and $MgH_2O_2$; which does not, however, take place in presence of an alkaline chlorid, or of certain organic matters, such as sugar and gum. Many organic substances decompose it into $(Hg_2)Cl_2$ or Hg, especially under the influence of sunlight. Thus in sunlight it is reduced by oxalic acid, which is itself oxidized to carbon dioxid: $2HgCl_2+C_2O_4H_2=Hg_2Cl_2+2CO_2+2HCl$. For this reason it behaves as an oxidant: $2HgCl_2+H_2O=Hg_2Cl_2+2HCl+O$. Albumen forms with it a white precipitate, which is insoluble in $H_2O$, but soluble in an excess of fluid albumen and in solutions of alkaline chlorids. It readily combines with metallic chlorids, to form soluble double chlorids, called **chloromercurates** or **chlorhydrargyrates.** One of these, obtained in flattened, rhombic prisms, by the cooling of a boiling solution of $HgCl_2$ and $NH_4Cl$, has the composition $Hg(NH_4)_2Cl_2+Aq$, and was formerly known as *sal alembroth* or *sal sapientiæ*. It is a very energetic germicide.

**Mercurammonium Chlorid**—*Mercury chloramidid*—*Infusible white precipitate*—*Ammoniated mercury*—**Hydrargyrum ammoniatum** (U. S.; Br.)—$NH_2HgCl$—251.8—is prepared by adding a slight excess of $NH_4HO$ to a solution of $HgCl_2$. It is a white powder, insoluble in alcohol, ether, and cold $H_2O$: decomposed by hot $H_2O$, with separation of a heavy, yellow powder. It is entirely volatile, without fusion. The *fusible white precipitate* is formed in small crystals when a solution containing equal parts of $HgCl_2$ and $NH_4Cl$ is decomposed by $Na_2CO_3$. It is **mercurdiammonium chlorid**, $NH_2Hg,NH_4Cl_2$.

**Iodids.**—**Mercurous Iodid**—*Protoiodid* or *yellow iodid*—**Hydrargyri iodidum viride** (U. S.; Br.)—$Hg_2I_2$—654.3—is prepared by grinding together 200 pts. Hg and 127 pts. I with a little alcohol, until a green paste is formed. It is a greenish-yellow, amorphous powder, insoluble in $H_2O$ and in alcohol. When heated, it turns brown, and volatilizes completely. When exposed to light, or even after a time in the dark, it is decomposed into $HgI_2$ and Hg. The same decomposition is brought about instantly by KI; more slowly by solutions of alkaline chlorids, and by HCl when heated. $NH_4HO$ dissolves it with separation of a gray precipitate.

**Mercuric Iodid**—*Biniodid* or *red iodid*—**Hydrargyri iodidum rubrum** (U. S.; Br.)—$HgI_2$—454—is obtained by double decomposition between $HgCl_2$ and KI, care being had to avoid too great an excess of the alkaline iodid, that the soluble potassium iodhydrargyrate may not be formed.

It is sparingly soluble in $H_2O$; but forms colorless solutions with alcohol. It dissolves readily in many dilute acids, and in solutions of

ammoniacal salts, alkaline chlorids, and mercuric salts; and in solutions of alkaline iodids. Iron and copper convert it into $(Hg_2)I_2$, then into Hg. The hydroxids of K and Na decompose it into oxid or oxyiodid, and combine with another portion to form iodhydrargyrates, which dissolve. $NH_4HO$ separates from its solution a brown powder, and forms a yellow solution, which deposits white flocks.

**Mercuric Cyanid — Hydrargyri cyanidum** (U. S.)— $Hg(CN)_2$—252.3—is best prepared by heating together, for a quarter of an hour, potassium ferrocyanid, 1 pt.; $HgSO_4$, 2 pts.; and $H_2O$, 8 pts. It crystallizes in quadrangular prisms; soluble in 8 pts. of $H_2O$, much less soluble in alcohol; highly poisonous. When heated dry it blackens, and is decomposed into $(CN)_2$ and Hg; if heated in presence of $H_2O$ it yields HCN, Hg, $CO_2$, and $NH_3$. Hot concentrated $H_2SO_4$, and HCl, HBr, HI, and $H_2S$ in the cold decompose it, with liberation of HCN. It is not decomposed by alkalies.

**Nitrates.**—There exist, besides the normal nitrates: $(Hg_2)(NO_3)_2$, and $Hg(NO_3)_2$, three basic mercurous nitrates, three basic mercuric nitrates, and a mercuroso-mercuric nitrate.

**Mercurous Nitrate**—$(Hg_2)(NO_3)_2+2Aq$—524.6+36—is formed when excess of Hg is digested with $HNO_3$, diluted with ½ vol. $H_2O$; until short, prismatic crystals separate.

It effloresces in air; fuses at 70° (158° F.); dissolves in a small quantity of hot $H_2O$, but with a larger quantity is decomposed with separation of the yellow, basic **trimercuric nitrate** $Hg(NO_3)_2,2HgO+Aq$.

**Dimercurous Nitrate**—$(Hg_2)(NO_3)_2$, $Hg_2O+Aq$—941.2+18—is formed by acting upon the preceding salt with cold $H_2O$ until it turns lemon-yellow; or by extracting with cold $H_2O$ the residue of evaporation of the product obtained by acting upon excess of Hg with concentrated $HNO_3$.

**Trimercurous Nitrate**—$(Hg_2)_2(NO_3)_4$, $Hg_2O+3Aq$—1465.8+54—is obtained in large, rhombic prisms, when excess of Hg is boiled with $HNO_3$, diluted with 5 pts. $H_2O$, for 5–6 hours, the loss by evaporation being made up from time to time.

**Mercuric Nitrate**—$Hg(NO_3)_2$—324.3—is formed when Hg or HgO is dissolved in excess of $HNO_3$, and the solution evaporated at a gentle heat. A syrupy liquid is obtained, which, over quicklime, deposits large, deliquescent crystals, having the composition $2[Hg(NO_3)_2]+Aq$, while there remains an uncrystallizable liquid, $Hg(NO_3)_2+2Aq$.

This salt is soluble in $H_2O$, and exists in the **Liq. hydrargyri nitratis** (U. S.), **Liq. hydrargyri nitratis acidus** (Br.); in the volumetric standard solution used in *Liebig's process* for urea; and probably in *citrine ointment*=**Ung. hydrar. nitratis** (U. S.; Br.).

**Dimercuric Nitrate**—$Hg(NO_3)_2$, $HgO+Aq$—540.6—is formed when HgO is dissolved to saturation in hot $HNO_3$, diluted with 1 vol. $H_2O$; and crystallizes on cooling. It is decomposed by $H_2O$ into **trimercuric nitrate**, $Hg(NO_3)_2$, $2HgO$, and $Hg(NO_3)_2$.

**Hexamercuric Nitrate**—$Hg(NO_3)_2$, $5HgO$—1405.8—is formed as a red powder, by the action of $H_2O$ on trimercuric nitrate.

**Sulfates.—Mercurous Sulfate**—$(Hg_2)SO_4$—495.4—is a white, crystalline powder, formed by gently heating together 2 pts. Hg and 3 pts. $H_2SO_4$, and causing the product to combine with 2 pts. Hg. Heated with NaCl it forms $(Hg_2)Cl_2$.

**Mercuric Sulfate—Hydrargyri sulfas** (Br.)—$HgSO_4$—296.3—is obtained by heating together Hg and $H_2SO_4$, or Hg, $H_2SO_4$, and $HNO_3$. It is a white, crystalline, anhydrous powder, which, on contact with $H_2O$, is decomposed with formation of **trimercuric sulfate**, $HgSO_4$, $2HgO$; a yellow, insoluble powder, known as **turpeth mineral=Hydrargyri subsulfas flavus** (U. S.).

**Analytical Characters.**—MERCUROUS.—(1) Hydrochloric acid: white ppt.; insoluble in $H_2O$ and in acids; turns black with $NH_4HO$; when boiled with HCl, deposits Hg, while $HgCl_2$ dissolves. (2) Hydrogen sulfid: black ppt.; insoluble in alkaline sulfhydrates, in dilute acids, and in KCN; partly soluble in boiling $HNO_3$. (3) Potash: black ppt.; insoluble in excess. (4) Potassium iodid: greenish ppt.; converted by excess into Hg, which is deposited, and $HgI_2$, which dissolves.

MERCURIC.—(1) Hydrogen sulfid: black ppt. If the reagent be slowly added, the ppt. is first white, then orange, finally black. (2) Ammonium sulfhydrate: black ppt.; insoluble in excess, except in the presence of organic matter. (3) Potash or soda: yellow ppt.; insoluble in excess. (4) Ammonium hydroxid: white ppt.; soluble in great excess and in solutions of $NH_4$ salts. (5) Potassium carbonate: red ppt. (6) Potassium iodid: yellow ppt., rapidly turning to salmon color, then to red; easily soluble in excess of KI, or in great excess of mercuric salt. (7) Stannous chlorid, in small quantity: white ppt.; in larger quantity: gray ppt.; and when boiled: deposit of globules of Hg.

**Action on the Economy.**—Mercury, in the metallic form, is without action upon the animal economy so long as it remains such. On contact, however, with alkaline chlorids it is converted into a soluble double chlorid, and this the more readily the greater the degree of subdivision of the metal. The mercurials insoluble in dilute HCl are also inert until they are converted into soluble compounds.

Mercuric chlorid, a substance into which many other compounds of Hg are converted when taken into the stomach or applied to the skin, not only has a distinctly corrosive action, by virtue of its ten-

dency to unite with protein bodies, but, when absorbed, it produces well-marked poisonous effects, somewhat similar to those of arsenical poisoning. Indeed, owing to its corrosive action, and to its greater solubility and more rapid absorption, it is a more dangerous poison than $As_2O_3$. In poisoning by $HgCl_2$, the symptoms begin sooner after the ingestion of the poison than in arsenical poisoning, and those phenomena referable to the local action of the toxic are more intense. But the entire duration of the poisoning is greater, In fatal cases, death usually occurs in 5 to 12 days.

The treatment should consist in the administration of white of egg, not in too great quantity, and the removal of the compound formed, by emesis, before it has had time to redissolve in the alkaline chlorids contained in the stomach.

Absorbed Hg tends to remain in the system in combination with protein bodies, from which it may be set free, or, more properly, brought into soluble combination, at a period quite removed from the date of last administration, by the exhibition of alkaline iodids.

Mercury is eliminated principally by the saliva and urine, in which it may be readily detected. The fluid is faintly acidulated with HCl, and in it is immersed a short bar of Zn, around which a spiral of dentist's gold foil is wound in such a way as to expose alternate surfaces of Zn and Au. After 24 hours, if the saliva or urine contain Hg, the Au will be whitened by amalgamation; and, if dried and heated in the closed end of a small glass tube, will give off Hg, which condenses in globules, visible with the aid of a magnifier, in the cold part of the tube.

# ORGANIC CHEMISTRY.

## COMPOUNDS OF CARBON.

In the beginning of the present century chemistry was divided into the two sections of **inorganic** and **organic**. The former treated of the products of the mineral world, the latter of substances produced in *organized* bodies, vegetable or animal. This subdivision, originally made upon the supposition that organic substances could only be produced by "vital processes," is retained only for convenience and because of the great number of the carbon compounds.

When it was found that organic substances were made up of a very few elements, and that they all contained carbon, Gmelin proposed to consider as organic substances all such as contained more than one atom of C, his object in thus limiting the minimum number of C atoms being that substances containing one atom of C, such as carbon dioxid and marsh gas, are formed in the mineral kingdom, and consequently, according to then existing views, could not be considered as *organic*. Such a distinction, still adhered to in text-books of very recent date, of necessity leads to most incongruous results. Under it the first terms of the homologous series (see p. 218) of saturated hydrocarbons, $CH_4$, alcohols, $CH_4O$, acids, $CH_2O_2$, and all their derivatives are classed among mineral substances, while all the higher terms of the same series are organic. Under it urea, $CON_2H_4$, the chief product of excretion of the animal body, is a mineral substance, but ethene, $C_2H_4$, obtained from the distillation of coal, is organic.

The idea of organic chemistry conveyed by the definition: "that branch of the science of chemistry which treats of the carbon compounds containing hydrogen," is still more fantastic. Under it hydrocyanic acid, CNH, is "organic," but the cyanids, CNK, are "mineral." Oxalic acid, $C_2O_4H_2$, is "organic," and potassium hydroxid, KHO, unquestionably "mineral." If these two act upon each other in the proportion of 90 parts of the former to 56 of the latter, the "organic" monopotassic oxalate, $C_2O_4HK$, is formed, but if the proportion of KHO be doubled, other conditions remaining the same, the "mineral" dipotassic oxalate, $C_2O_4K_2$, is produced. Similarly one of the sodium carbonates, $Na_2CO_3$, is "mineral;" the other, $NaHCO_3$, is "organic."

The notion that organic substances could only be formed by some mysterious agency, manifested only in organized beings, was finally exploded by the labors of Wöhler and Kolbe. The former obtained urea from ammonium cyanate (1828); while the latter, at a subse-

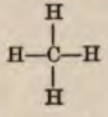
quent period, formed acetic acid, using in its preparation only such unmistakably mineral substances as coal, sulfur, aqua regia, and water. Since Wöhler's first synthesis, chemists have succeeded not only in making from mineral materials many of the substances previously only formed in the laboratory of nature, but have also produced a vast number of carbon compounds which were previously unknown, and which, so far as we know, have no existence in nature.

At the present time, therefore, **we must consider as an organic substance any compound containing carbon, whatever may be its origin and whatever its properties.**

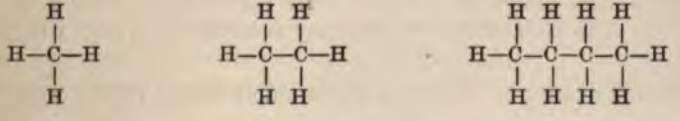
Organic chemistry is, therefore, simply the chemistry of the carbon compounds. In the study of the compounds of the other elements, we have to deal with a small number of substances, relatively speaking, formed by the union with each other of a large number of elements. With the organic substances the reverse is the case. Although compounds have been formed which contain C along with each of the other elements, the great majority of the organic substances are made up of C, combined with a very few other elements; H, O, and N occurring in them most frequently.

It is chiefly in the study of the carbon compounds that we have to deal with **radicals** (see p. 52). Among mineral substances there are many whose molecules consist simply of a combination of two atoms. Among organic substances there is none which does not contain a radical: indeed, organic chemistry has been defined as "the chemistry of compound radicals."

The atoms of carbon possess in a higher degree than those of any other element the power of uniting with each other, and in so doing of interchanging valences. Were it not for this property of the C atoms, we could have but one saturated compound of carbon and hydrogen, $CH_4$, or expressed graphically:



There exist, however, a great number of such compounds, which differ from each other by one atom of C and two atoms of H. In these substances the atoms of C may be considered as linked together in a continuous chain, their free valences being satisfied by H atoms, thus:



**Homologous Series.**—It will be observed that these formulæ differ from each other by $CH_2$, or some multiple of $CH_2$, more or less. In examining numbers of organic substances which are closely related to each other in their properties, we find that we can arrange the great majority of them in series, each term of which differs from the one below it by $CH_2$; such a series is called an **homologous series.** It will be readily understood that such an arrangement in series vastly facilitates the remembering of the composition of organic bodies. In the following table, for example, are given the saturated hydrocarbons, and their more immediate derivatives. At the head of each vertical column is an **algebraic formula,** which is the **general formula** of the entire series below it; $n$ being equal to the numerical position in the series.

HOMOLOGOUS SERIES.

| Saturated hydrocarbons, $C_nH_{2n+2}$ | Alcohols, $C_nH_{2n+2}O$ | Aldehydes $C_nH_{2n}O$ | Acids, $C_nH_{2n}O_2$ | Ketones, $C_nH_{2n}O$ |
|---|---|---|---|---|
| $CH_4$ | $CH_4O$ | $CH_2O$ | $CO_2H_2$ | . . . . |
| $C_2H_6$ | $C_2H_6O$ | $C_2H_4O$ | $C_2O_2H_4$ | . . . . |
| $C_3H_8$ | $C_3H_8O$ | $C_3H_6O$ | $C_3O_2H_6$ | $C_3H_6O$ |
| $C_4H_{10}$ | $C_4H_{10}O$ | $C_4H_8O$ | $C_4O_2H_8$ | $C_4H_8O$ |
| $C_5H_{12}$ | $C_5H_{12}O$ | $C_5H_{10}O$ | $C_5O_2H_{10}$ | $C_5H_{10}O$ |
| $C_6H_{14}$ | $C_6H_{14}O$ | $C_6H_{12}O$ | $C_6O_2H_{12}$ | . . . . |
| $C_7H_{16}$ | $C_7H_{16}O$ | $C_7H_{14}O$ | $C_7O_2H_{14}$ | . . . . |
| $C_8H_{18}$ | $C_8H_{18}O$ | $C_8H_{16}O$ | $C_8O_2H_{16}$ | . . . . |
| $C_9H_{20}$ | $C_9H_{20}O$ | . . . . | $C_9O_2H_{18}$ | . . . . |
| $C_{10}H_{22}$ | $C_{10}H_{22}O$ | . . . . | $C_{10}O_2H_{20}$ | . . . . |
| $C_{11}H_{24}$ | . . . . | . . . . | . . . . | . . . . |
| $C_{12}H_{26}$ | . . . . | . . . . | $C_{12}O_2H_{24}$ | . . . . |
| $C_{13}H_{28}$ | . . . . | . . . . | . . . . | . . . . |
| $C_{14}H_{30}$ | . . . . | . . . . | $C_{14}O_2H_{28}$ | . . . . |

But the arrangement in homologous series does more for us than this. The properties of substances in the same series are similar, or vary in regular gradation according to their position in the series. Thus, in the series of monoatomic alcohols (see above) each member yields on oxidation, first an aldehyde, then an acid. Each yields a series of compound ethers by the action of acids upon it. The boiling-points of ethylic alcohol and its seven superior homologues are: 78.3°, 97.4°, 116.8° 137°, 157°, 176°, 195°, from which it will be seen that the boiling-point of any one of them can be determined, with a maximum error of less than 1°, by taking the mean of those of its neighbors above and below. In this way we may predict, to some extent, the properties of a wanting member in a series before its discovery.

The terms of any homologous series must all have the same con-

stitution, i. e., their constituent atoms must be similarly arranged within the molecule. (See p. 53.)

**Isomerism—Metamerism—Polymerism.—Two substances are said to be isomeric, or to be isomeres of each other, when they have the same centesimal composition.** If, for instance, we analyze acetic acid, formic aldehyde and methyl formate, we find that each body consists of C, O and H, in the following proportions:

| | | | |
|---|---|---|---|
| Carbon | 40 | = | 12 |
| Oxygen | 53.33 | = | 16 |
| Hydrogen | 6.67 | = | 2 |
| | 100.00 | | 30 |

This identity of percentage composition may occur in two ways. The three substances may each contain the same number of each kind of atom in a molecule; or they may contain in their several molecules the same kinds of atoms in multiple proportions. In the above example each substance may have the formula, $CH_2O$; or one may have that formula and the others $C_2H_4O_2$, $C_3H_6O_3$, $C_4H_8O_4$, $C_5H_{10}O_5$, etc.

**When two or more substances have the same percentage composition and the same molecular weight they are said to be metameric. When they have the same percentage composition and their molecular weights are simple multiples of the lowest molecular weight represented by that percentage composition, they are said to be polymeric.**

Other conditions of isomerism will be considered later (see space isomerism, p. 266, and place isomerism, pp. 290, 381).

In order to determine the composition (the empirical formula) of an organic substance, two factors are therefore necessary: the percentage composition and the molecular weight.

**Elementary Organic Analysis.**—The first step in an analysis to determine the composition of an organic substance is a qualitative analysis to identify the elements existing in the molecule. This having been done, the quantitative analysis is next in order.

The simplest case is where the substance is a hydrocarbon, i. e., a compound of carbon and hydrogen only. The determination of both elements is made in one operation, by taking advantage of the fact that when a compound containing carbon and hydrogen is heated with cupric oxid all the carbon is converted into $CO_2$, and all the hydrogen into $H_2O$. Thus, if $C_2H_6O+6CuO=2CO_2+3H_2O+6Cu$, 46 parts of alcohol will produce 88 pts. of carbon dioxid and 54 pts. of water. The apparatus required consists of a tube of difficultly fusible glass, called a combustion tube, about 60 cent. long, drawn out to a point and closed at one end, a "combustion furnace," in which this tube may be heated, and the absorbing apparatus referred to below.

A weighed quantity of the substance of which a "combustion" is to be made (sealed in a small glass bulb if liquid) is placed in the closed end of the combustion tube, *a* Fig. 32, along with the requisite quantity of recently ignited cupric oxid, leaving space for the passage of the gases produced. The tube is then placed in the furnace and its open end connected with a U tube, *b*, filled with fused $CaCl_2$, or with fragments of pumice moistened with concentrated $H_2SO_4$, whose weight has been determined, and whose purpose it is to absorb the $H_2O$ produced. This first U tube is connected with a "Liebig's bulb" containing a strong solution of KHO, *c*, and this in turn with another U tube in all respects similar to the first, *d*, both *c* and *d* having been previously weighed. The purpose of *c* is to absorb the $CO_2$ produced, that of *d* to retain water carried over from *c* by the current of gas. The combustion tube is then carefully heated until the evolution of gases ceases, when the closed, drawn-out end of the tube is broken and connected with a gasometer containing pure, dry oxygen, a cur-

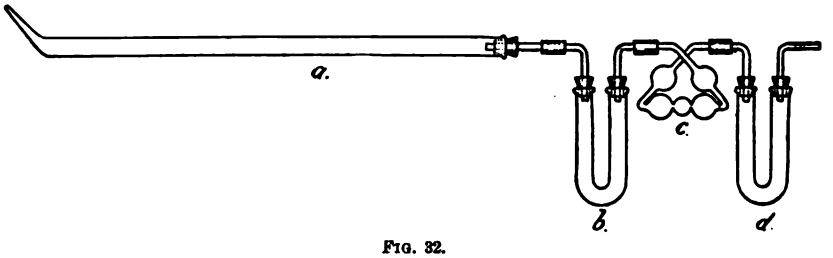



FIG. 32.

rent of which is passed slowly through the apparatus to bring the last portions of the products of combustion into the absorbing apparatus. Finally the U tubes and the KHO bulb are again weighed. The increase in weight of *b* is the weight of $H_2O$ produced, every 9 parts of which represent 1 part of H. The increase in weight of *c* and *d* is the weight of $CO_2$ produced, every 44 parts of which represent 12 parts of C. If the substance analyzed contain N, Cl, Br or I, a heated column of pure metallic Cu is interposed toward the open end of the combustion tube, to reduce any oxids of N produced to N, and to retain the Cl, Br or I. If the substance contain S, a layer of lead peroxid is similarly placed to retain the S as $PbSO_4$.

If the substance consist of C, H and O, the C and H are determined in the manner above described, and the difference between the sum of their weights and that of the substance burnt is the amount of O.

Nitrogen is most readily determined by the method of Kjeldahl. A known weight of the substance is dissolved by heating it in concentrated $H_2SO_4$. Potassium permanganate is then added until the mix-

ture is green. The N contained in the substance is thus converted into ammonia. The strongly acid liquid is diluted, rendered alkaline by addition of NaHO, and the $NH_3$ is distilled over into a receiver containing a known quantity of acid. The amount of $NH_3$ produced is calculated from the amount of acid neutralized, and every 17 parts of $NH_3$ represent 14 parts of N. In the analysis of nitro- and cyanogen compounds sugar is added, and in that of nitrates, benzoic acid.

Two other methods of determining N are in general use: That of Dumas, in which the substance is burnt in a manner very similar to that above described, and the N produced is collected and measured. The weight of N is then calculated from the volume, with the necessary corrections for variations of temperature and pressure. In the method of Will and Varrentrap the N of the compound is converted into $NH_3$ by heating with a caustic alkali, and the amount of $NH_3$ is determined as in Kjeldahl's method. For the details of these processes and for methods of determination of other elements in organic compounds the student is referred to works on quantitative analysis, such as that of Fresenius. The details of the directions must be rigidly observed to avoid error.

**Determination of Molecular Weights.**—The percentage composition having been determined, the simplest corresponding ratio of the atoms in the molecule is obtained by dividing the percentage of each element by its atomic weight. Thus if analyses be made of formic aldehyde, acetic acid, methyl formate, lactic acid and glucose, the results in each case will be:

| | | | |
|---|---|---|---|
| Carbon | 40.00 per cent. | ÷12 | = 3.33 = 1 |
| Hydrogen | 6.67 " " | ÷ 1 | = 6.67 = 2 |
| Oxygen | 53.33 " " | ÷16 | = 3.33 = 1 |

and the simplest empirical formula of all of the substances mentioned is therefore $CH_2O$. The molecular weight of formic aldehyde is 30; its formula is therefore $CH_2O$ (12+2+16). The molecular weights of acetic acid and of methyl formate are 60: they, therefore, each have the formula $C_2H_4O_2$. The molecular weight of lactic acid is 90 and that of glucose 180: the formula of the former is, therefore, $C_3H_6O_3$, and that of the latter $C_6H_{12}O_6$.

If the substance be one which can be vaporized without decomposition, its molecular weight is derived from its specific gravity as referred to hydrogen in the manner already described (p. 38). The process for determining the specific gravity now generally adopted is that of Victor Meyer. (See Ganot's Physics, 15th Am. Ed., p. 381, or other works upon that subject.)

Three other physical methods of determining molecular weights are available:

1. *From Osmotic Pressure.*—It has been stated (p. 20) that substances in solution exert a pressure equal to that which would be exerted by an equal amount of the substance, if it were converted into gas, and occupied the same volume, at the same temperature, as the solution. Therefore the law of Avogadro has the same value for solutions as for gases, and equal volumes of solutions exerting equal osmotic pressures at the same temperature contain equal numbers of molecules. Applying this fact in the same manner as the law of Avogadro is applied in the case of gases, the molecular weight may be derived from the osmotic pressure by the formula:

$$M=\frac{a.6218\ (273+t)}{P}$$

in which M=the molecular weight; a=the weight of dissolved substance in 1 cc., expressed in grams; t=the observed temperature; and P=the osmotic pressure. The solutions used must be dilute, and the "semi-permeable" membrane used is either a living plant cell or an artificial membrane of copper ferrocyanid.

2. *From Elevation of the Boiling Point.*—Solutions have a lower vapor pressure than the pure solvent at the same temperature, and consequently the former boil at a higher temperature than the latter. The elevation of the boiling point is proportionate to the quantity of substance dissolved, if that substance be non-volatile. If molecular quantities be considered, it is found that equal elevations are observed with solutions containing equal molecular weights of different substances in the same volume of solvent. And, with different solvents, the elevations are equal when the same quantity of substance is dissolved in molecular quantities of the several solvents.

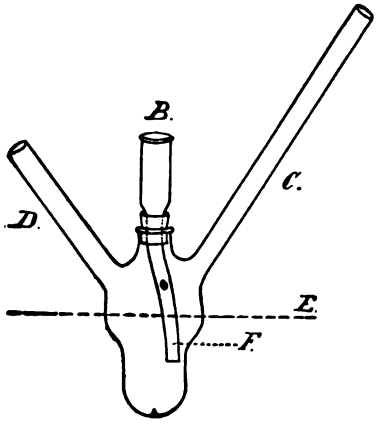


FIG. 33.

Beckman's method is the one generally used: The special apparatus used consists of a peculiarly-shaped boiling flask (Fig. 33) and a very delicate thermometer. The body of the flask is filled with glass pearls to within 1 cm. of the lower opening of the condensor tube *f*. The flask, with stoppers in the three openings, is first weighed. The solvent is then introduced to the level *e*, and the flask reweighed. The difference is the weight of the solvent used.

The flask is then mounted, surrounded by an asbestos mantle, in a position to be heated; the thermometer is adjusted in the neck *d* with its bulb immersed in the solvent; the neck *b* is connected with a condenser. The solvent is then boiled and the temperature noted. A known weight of the substance is then introduced through the neck *c* and the boiling point again noted. The molecular weight is calculated by the formula: $m=\text{p}.\frac{\text{d}}{\text{d}^1}$; in which p=the weight in grams of substance dissolved in 100 cc.; d=the molecular rise in boiling point of the solvent; and $\text{d}^1$=the observed rise in boiling point. The value of d is determined by the formula: $\text{d}=0.02.\frac{\text{t}^2}{\text{w}}$; in which t=the absolute boiling point, and w=the heat of evaporation of the solvent. For ether the value of d is 21.1°, for chloroform 36.6°, and for acetic acid 25.3°.

3. *From the Depression of the Freezing Point.*—The law of Raoult (see p. 17) is utilized to determine molecular weights. Various forms of apparatus are used, in all of which the freezing point of the solvent is first determined, and then that of the same liquid after addition of a known weight of the substance. The molecular weight is calculated by the formula: $\text{m}=\frac{\text{pt}}{\text{c}}$; in which t=the constant for the solvent used; p=the weight in grams of the substance dissolved in 100 grams of the solvent; and c=the depression observed.

4. *Chemical Methods* are also resorted to to determine molecular weights. They consist in producing derivatives, which are then analyzed and the results thus obtained compared with the formulæ deducible from the analysis of the original compound. These methods are sometimes exceedingly complicated, in other cases very simple. When the substance is a base or an acid it is converted into a mineral ester or into a salt, and the combined mineral acid or metal is determined. For example: Acetic acid and lactic acid both have the percentage composition C=40.00%, H=6.67%, O=53.33%, corresponding to the formula $CH_2O$, or some multiple thereof. The atomic weight of silver is 107.7. If the two acids are converted into their silver salts, and the amount of silver in each determined, the acetate will be found to contain 64.6% of silver, and the lactate 54.8%. If both acids are monobasic the former percentage of silver corresponds to the formula $C_2H_3O_2Ag$, and the latter to the formula $C_3H_5O_3Ag$.

The basicity of the acid is determined by measuring the increase of molecular conductivity (p. 44) of solutions of the sodium salt of the acid with increasing dilution. With the sodium salts of monobasic acids this increase is from 10 to 13 units with dilution of 32–1024 litres for the equivalent of the substance, with sodium salts of

dibasic acids 28 to 31, with those of tetrabasic acids about 40, and with those of pentabasic acids about 50 units.

**Determination of Constitution.**—The properties of organic compounds depend, therefore, not only upon their composition, but also upon their constitution, i. e., upon the arrangement of the atoms in the molecule (see p. 53). The constitution of a substance is determined by a study of the methods of its formation, of the products of its decomposition, and of substances produced by the introduction of other elements or groups into its molecule. A statement of the more important principles, and one or two examples, must suffice here.

The carbon atom is quadrivalent in almost all, if not in all organic compounds. In the few in which it is considered as bivalent, as in carbon monoxid, CO, and the isonitrils, $(C_2H_5)—N=C$, the oxygen may be considered to be quadrivalent, and the nitrogen quinquivalent, in which case the carbon would be quadrivalent.

The carbon atoms may unite with each other in three ways: (1) Two carbon atoms may exchange a single valence in their union, forming a hexavalent group, $\equiv C—C\equiv$; (2) they may unite with exchange of two valences, forming a quadrivalent group, $=C=C=$; or, (3) they may unite with exchange of three valences, forming a bivalent group, $—C\equiv C—$. These are referred to as **single, double and treble linkages**, respectively.

Only those compounds in which all of the linkages are single are **saturated compounds**, i. e., compounds in which all of the possible valences of the constituent atoms are satisfied. Compounds containing two or more carbon atoms doubly or trebly linked are **unsaturated.**

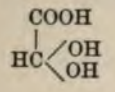
Other atoms or radicals can be introduced into a saturated molecule only by **substitution**, i. e., by causing them to take the place of other atoms or radicals of equivalent valence, removed at the same time. Thus when chloroform (itself a derivative of marsh gas, $CH_4$) is converted into tetrachlorid, the remaining hydrogen is removed as hydrochloric acid $CHCl_3+Cl_2=CCl_4+HCl$.

Unsaturated compounds may be similarly modified both by substitution and also by **addition.** In the latter case the double or treble linkage is reduced to a single or double one. Thus ethylene may yield ethylene chlorid by the addition: $H_2C:CH_2+Cl_2=ClH_2C.CH_2Cl$; or, by addition and substitution, carbon hexachlorid: $H_2C:CH_2+5Cl_2=Cl_3C.CCl_3+4HCl$.

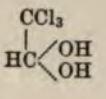
In the above substitutions the chlorin is not only added to the molecule operated upon; it also removes hydrogen by combining with it. Similarly, in oxidations O removes $H_2$, as when alcohol is oxidized to acetic acid: $C_2H_6O+O_2=C_2H_4O_2+H_2O$. Consequently in oxidations

an even number of hydrogen atoms is always removed. The tendency to the formation of water is so strong that in reactions in which two or more hydroxyl groups should unite with the same carbon atom, water almost invariably splits off and oxygen unites doubly with the carbon. Thus caustic potash does not act upon ethidene chlorid to produce a glycol according to the equation $CH_3.CHCl_2 + 2KHO = CH_3.CH(OH)_2 + 2KCl$, but to produce an aldehyde according to the equation, $CH_3.CHCl_2 + 2KHO = CH_3.CHO + H_2O + 2KCl$.

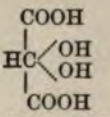
Exceptions to this rule occur when the carbon atom is linked to another carbon atom contained in a highly oxidized or halide group, as in the compounds:



Glyoxalic acid.



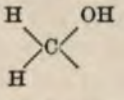
Chloral hydrate.



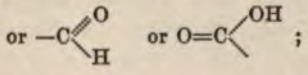
Mesoxalic acid.

Usually when an atom or group replaces another in a compound it occupies the position vacated by that which is removed, as when alcohol is formed by the action of caustic potash upon ethyl iodid: $CH_3.CH_2I + KHO = CH_3.CH_2OH + KI$. There is an exception to this rule when an unsaturated compound may yield either another unsaturated compound in obedience to the rule or an isomeric saturated compound in violation to it, the more stable saturated compound is formed. Thus the hydration of vinyl bromid, $CH_2:CHBr$, does not produce vinyl alcohol, $CH_2:CHOH$, but its isomere: aldehyde, $CH_3.CHO$. Indeed unsaturated compounds are frequently converted into saturated isomeres by intramolecular transposition of atoms by mere application of heat.

The genesis of ethylic alcohol from the action of caustic potash upon ethyl iodid: $CH_3.CH_2I + KHO = CH_3.CH_2OH + KI$, shows that the alcohol contains the univalent group $CH_2OH$, or



which, on oxidation, may lose two atoms of hydrogen with formation of either one of the two univalent groups CHO, or COOH;



which occur in the products of oxidation of ethylic alcohol: aldehyde and acetic acid.

The groups $CH_2OH$, CHO and COOH, referred to above, are examples of the so-called **characterizing groups** which exist in the

molecules of different classes of substances. The following are the more commonly recurring characterizing groups, and the classes of substances in which they occur:

| | | |
|---|---|---|
| $(CH_2OH)'$ | $= \begin{matrix} H \\ HO \end{matrix}\!\!>\!C\!<\!\!\begin{matrix} H \\ \end{matrix}$ | in primary alcohols, |
| $(CHOH)''$ | $= \begin{matrix} H \\ HO \end{matrix}\!\!>\!C=$ | " secondary alcohols, |
| $(COH)'''$ | $= \vdots C.OH$ | " tertiary alcohols, |
| $(CHO)'$ | $= O=C\!<\!\!\begin{matrix} H \\ \end{matrix}$ | " aldehydes, |
| $(CO)''$ | $= O:C:$ | " ketones, called *carbonyl*,* |
| $(COOH)'$ | $= O=C\!<\!\!\begin{matrix} OH \\ \end{matrix}$ | " acids, called *carboxyl*, |
| $(SO_2OH)'$ | $= \begin{matrix} O \\ O \end{matrix}\!\!>\!S\!<\!\!\begin{matrix} OH \\ \end{matrix}$ | " sulfonic acids, |
| $(NH_2)'$ | $= H_2:N.$ | " amido compounds, |
| $(NH)''$ | $= H.N:$ | " imido compounds, |
| $(NO_2)'$ | $= \begin{matrix} O \\ O \end{matrix}\!\!>\!N-$ | " nitro compounds, |
| $(NO)'$ | $= O:N.$ | " nitroso compounds. |

**Nomenclature of Organic Compounds.**—The vast number and great variety of structure of organic compounds make it difficult to devise a system of nomenclature which will apply to the more complex derivatives without producing names which are most complicated and difficult of pronunciation. Indeed, in view of the constantly increasing number of carbon compounds, no complete system of nomenclature is as yet possible. The most recent attempt to formulate one is that of the Geneva Commission of 1892. In this system the names of the hydrocarbons serve as the roots from which the names of their derivatives are constructed by the addition of syllables indicating the function (see p. 42) of the substance. Thus the alcohols are indicated by the syllable *ol*, the aldehydes by *al*, the ketones by *on*, and the acids by the word *acid*. The "Geneva" name of ethylic alcohol would be *ethanol*, that of acetic aldehyde *ethanal* and that of acetic acid *ethan-acid*. These names have not come into general use.

In the nomenclature generally followed the name of a substance is made up of the name of that of the class, or "function," to which the substance belongs, as *acid*, *alcohol*, *ketone*, *ester*, etc., to which are added a qualifying word derived from the origin of the body, as *lactic* acid, *acetic* acid, etc., or from its composition, as *methylic* alcohol, *ethylic* ether, etc., and the names of any radicals which have been introduced into the molecule of the parent compound. Thus the

*This group also exists in other compounds, as in the aldehydes and acids in the manner indicated in the text, and in compounds, such as carbonyl chlorid, $COCl_2$, urea, $NH_2.CO.NH_2$, etc.

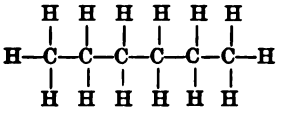
name of the substance $COOH.CH_2$ ($NH.CH_3$) is *methyl-amido-acetic acid*, in which "*acetic acid*" indicates that it is derived from acetic acid, $COOH.CH_3$, the syllable *amido* that $NH_2$ has been substituted for H in the $CH_3$ of the acid, and *methyl* that $CH_3$ has been substituted for H in $NH_2$.

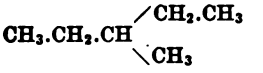
The names of the univalent radicals terminate in *yl*, as *methyl* $(CH_3)'$, *ethyl* $(C_2H_5)'$, *acetyl* $(C_2H_3O)'$, etc. Those of bivalent radicals terminate in *ene*, as *methylene*, $(CH_2)''$, *ethidene* $(C_2H_4)''$, etc., and those of the trivalent radicals in *enyl* or in *ine*, as *methenyl* or *methine* $(CH)'''$, *ethenyl* or *ethine* $(C_2H_3)'''$, etc.

**Classification of the Carbon Compounds.** — The hydrocarbons, consisting of carbon and hydrogen only, constitute the framework of the classification adopted, all other carbon compounds being considered as derivable from the hydrocarbons by substitution or by addition.

Carbon compounds are divided into two great classes, differentiated by the manner in which the carbon atoms are linked together:

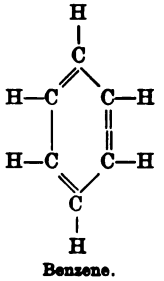
A. OPEN CHAIN COMPOUNDS, also called *acyclic*, *fatty*, or *aliphatic* (ἄλειφαρ=fat) compounds. In these compounds the carbon atoms are attached to each other in an open or arborescent chain, in which two or more carbon atoms are linked to but one other carbon atom, as in the compounds:



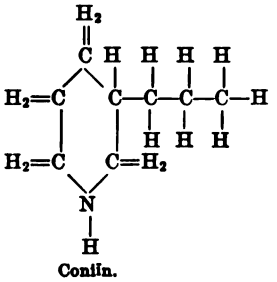


In the hydrocarbons of this class the number of hydrogen atoms, or this number, plus the number of univalent atoms that can be introduced into the molecule by addition, is equal to twice the number of carbon atoms plus two.

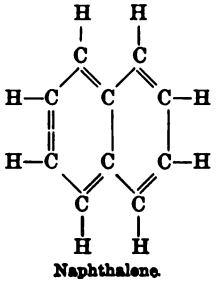
B. CLOSED CHAIN COMPOUNDS, also called *cyclic* or *aromatic* compounds. These compounds contain one or more closed *chains*, *rings*, or *nuclei* in which each carbon atom is linked to at least two other carbon atoms, or their equivalent, as in the compounds:



Benzene.



Coniin.



Naphthalene.

The closed chain compounds are subdivided into two classes:

I. *Carbocyclic compounds*, in which the ring or rings consist of carbon atoms exclusively, as in benzene and naphthalene, and

II. *Heterocyclic compounds*, in which atoms of elements other than carbon enter into the composition of the ring, as in coniïn.

# OPEN CHAIN, ALIPHATIC, ACYCLIC OR FATTY COMPOUNDS.

## HYDROCARBONS.

Six series are known:

**A. Methane, or Paraffin Series.** These are saturated compounds and have the algebraic formula, $C_nH_{2n+2}$. Their names terminate in "ane," e. g., Butane, $CH_3.CH_2.CH_2.CH_3$.

**B. Olefin Series,** containing two doubly-linked carbon atoms. General formula $C_nH_{2n}$. Their names terminate in "ene," e. g., Butene, $CH_2{:}CH.CH_2.CH_3$.

**C. Acetylene Series,** containing two trebly-linked carbon atoms. Algebraic formula, $C_nH_{2n-2}$. Their names terminate in "ine," e. g., Propine, $CH{:}C.CH_3$.

**D. Diolefin Series,** containing two pairs of doubly-linked carbon atoms. Algebraic formula, $C_nH_{2n-2}$, isomeric with the members of the acetylene series. Their names terminate in "diëne," e. g., Propadiëne, $CH_2{:}C{:}CH_2$.

**E. Olefin-acetylene Series,** containing both doubly- and trebly-linked carbon atoms. General formula, $C_nH_{2n-4}$. Their names terminate in "one," eg., Butone, $H_2C{:}CH.C{:}CH$.

**F. Diacetylene Series,** containing two pairs of trebly-linked carbon atoms. Algebraic formula, $C_nH_{2n-6}$. Their names are constructed by prefixing the syllable "di" to the name of the hydrocarbon of series C, from which they are derivable by fusion and elimination of $H_2$ or its equivalent, e. g., Diacetylene, $HC{:}C.C{:}CH$. The sixth terms, of which there are two isomeres: Dipropargyl, $HC{:}C.CH_2.CH_2.C{:}CH$, and Dimethyl diacetylene, $H_3C.C{:}C.C{:}C.CH_3$, are isomeric with benzene, the most important of the closed chain hydrocarbons.

# SATURATED COMPOUNDS—METHANE SERIES.

## HYDROCARBONS.

The saturated hydrocarbons at present known extend in unbroken series from methane, $CH_4$, to tetracosane, $C_{24}H_{50}$; and above that some members are known as high as dimyricyl, $C_{60}H_{122}$. The algebraic formula of the series is $C_nH_{2n+2}$. They are called **paraffins** because of their great stability (*parum*=little, *affinis*=affinity); and

also **alkanes.** They are also considered as the **hydrids** of the alcoholic radicals, $C_nH_{2n+1}$, methyl, ethyl, etc., which are called **alkyls.**

In the higher terms of the series, above the third, there exist two or more isomeres, increasing progressively in number with an increasing number of carbon atoms. Thus there are three having the empirical formula, $C_5H_{12}$:

(1) $CH_3.CH_2.CH_2.CH_2.CH_3$,
(2) $(CH_3)_2CH.CH_2.CH_3$, and, (3) $(CH_3)_4C$.

Hydrocarbons and their derivatives having the "unbranched" structure shown in formula (1) above, are designated as "normal" compounds; those derived from (2) are called "iso" compounds; and those derived from (3) "meso" compounds.

The number of possible isomeres increases rapidly with an increasing number of carbon atoms. It has been calculated that the number of possible isomeres with increasing values of $n$ are as follows:

| $n=1$ | $n=2$ | $n=3$ | $n=4$ | $n=5$ | $n=6$ |
|---|---|---|---|---|---|
| 1 | 1 | 1 | 2 | 3 | 5 |
| $n=7$ | $n=8$ | $n=9$ | $n=10$ | $n=11$ | $n=12$ |
| 9 | 18 | 35 | 75 | 159 | 357 |

Many of these hydrocarbons exist in nature, in petroleum, and in the gases accompanying it. They may be produced by the following general reactions:

(1) By the action of finely-divided zinc, silver or copper, or of sodium either alone, at elevated temperatures, or in the presence of $H_2O$, upon the corresponding iodids: $2C_2H_5I+Zn_2+2H_2O=ZnH_2O_2+ZnI_2+2C_2H_6$, or, $2C_2H_5I+Na_2=2NaI+C_4H_{10}$.

(2) By electrolysis of the corresponding fatty acid: $2C_2H_4O_2=2CO_2+C_2H_6+H_2$.

(3) By the action of the organo-zincic derivative upon the iodid of the alcoholic radical, upon the corresponding olefin iodid, or upon the allylic iodid (p. 371).

(4) By the action of highly concentrated hydriodic acid at 275°–300° (527°–572° F.) upon hydrocarbons of the ethene and ethine series, upon alcohols, amins, etc. This is a method of hydrogenation applicable in many other cases.

(5) By the destructive distillation of many organic substances.

**General Properties.**—They are gaseous, liquid, or solid, and have sp. gr. and boiling points increasing with the number of C atoms. The first four members are gaseous at the ordinary temperature, those above $C_{15}H_{32}$ are crystalline solids; the intermediate ones are colorless liquids. They are lighter than $H_2O$, neutral, insoluble in $H_2O$,

soluble in alcohol, ether, and in liquid hydrocarbons. Their odor is faint and not unpleasant.

They are very stable and incapable of modification by addition. Chlorin and bromin decompose them, with formation of products of substitution. They are inflammable and burn with a luminous flame. Nitric acid forms nitro-derivatives with the higher terms.

**Methyl Hydrid—Methane—Marsh-gas**—*Light carburetted hydrogen*—**Fire-damp**—$CH_4$—16—is given off in swamps as a product of decomposition of vegetable matter, in coal mines, and in the gases issuing from the earth in the vicinity of petroleum deposits. It is also formed during putrefaction of protein bodies and fermentation of carbohydrates. From these origins it exists in intestinal gases, sometimes to the extent of 26.5 per cent. Coal-gas contains it in the proportion of 36–50 per cent. It may be prepared by strongly heating a mixture of sodium acetate with sodium hydroxid and quicklime. Its complete synthesis, which is of theoretic interest, may be effected in several ways: (1) Carbon disulfid is first produced by passing vapor of sulfur over coal, heated to redness: $C+S_2=CS_2$. This may either be passed, along with hydrogen sulfid, over red-hot copper, when: $CS_2+2H_2S+8Cu=CH_4+4Cu_2S$, or, (2) it may be converted into carbon tetrachlorid by the reaction: $CS_2+3Cl_2=CCl_4+S_2Cl_2$; and this reduced by nascent hydrogen: $CCl_4+4H_2=CH_4+4HCl$. (3) Carbon monoxid, prepared by heating carbon in a limited quantity of air, is reduced by hydrogen when the two are treated with the induced electric current: $CO+3H_2=CH_4+H_2O$. (4) Aluminium carbid is decomposed by water according to the equation: $C_3Al_4+12H_2O=3CH_4+2Al_2(OH)_6$.

It is a colorless, odorless, tasteless gas; very sparingly soluble in $H_2O$; sp. gr. 0.559A. At high temperatures, it is decomposed into C and H. It burns in air with a pale yellow flame. Mixed with air or O it explodes violently on contact with flame, producing water and carbon dioxid; the latter constituting the **after-damp** of miners. It is not affected by Cl in the dark, but, under the influence of diffuse daylight, one or more of the H atoms are displaced by an equivalent quantity of Cl. In direct sunlight the substitution is accompanied by an explosion.

**Petroleum.**—Crude petroleum varies in color from a faintly yellowish tinge to a dark brown, nearly black, with greenish reflections. The lighter-colored varieties are limpid, and the more highly colored of the consistency of thin syrup. The sp. gr. varies from 0.74 to 0.92. Crude petroleums consist of normal paraffins (the lowest terms of the series being found in the gases accompanying petroleum and held in solution by the oil under the pressure it supports in natural pockets), besides hydrocarbons of the olefin, paraffene, and benzene

series. They also contain varying quantities of sulfur compounds, which communicate a disgusting odor to some oils.

The crude oil is highly inflammable, usually highly colored, and is prepared for its multitudinous uses in the arts by the processes of distillation and refining. The products of lowest boiling point are usually consumed, but are sometimes condensed.

The principal products of petroleum are: **Cymogene**, boils at 0° (32° F.), used in ice machines; **Rhigolene**, a highly inflammable liquid, sp. gr. about 0.60, boils at about 20° (68° F.), used to produce cold by its rapid evaporation. **Petroleum ether**, boils at 40°–70° (104°–158° F.), used as a solvent. **Gasolene**, boils from 45° (113° F.) to 76° (168.8° F.), used as a fuel and for the manufacture of "air gas." **Naphtha**, divided into three grades, C, B, and A, boils from 82.2° (180° F.) to 148.8° (300° F.), used as a solvent for fats, etc., and in the manufacture of "water gas." Sometimes called "safety oil." **Benzine, or benzolene**, boils from 148° (298° F.) to 160° (320° F.), used as a solvent in making paints and varnishes. The most important product of petroleum is that portion which distils between 176° (349° F.) and 218° (424° F.), and which constitutes **kerosene** and other oils used for burning in lamps. An oil to be safely used for burning in lamps should not "flash," or give off inflammable vapor, below 37.4° (100° F.), and should not burn at temperatures below 149° (300° F.). The better grades of kerosene have a flash point of from 110° F. to 150° F.

From the residue remaining after the separation of the kerosene, many other products are obtained. **Lubricating oils**, of too high boiling-point for use in lamps. **Paraffin**, a white, crystalline solid, fusible at 45°–65° (113°–149° F.), which is used in the arts for a variety of purposes formerly served by wax, such as the manufacture of candles. In the laboratory it is very useful for coating the glass stoppers of bottles, and for other purposes, as it is not affected by acids or by alkalies. It is odorless, tasteless, insoluble in $H_2O$ and in cold alcohol; soluble in boiling alcohol and in ether, fatty and volatile oils and mineral oils. It is also obtained by the distillation of certain varieties of coal, and is found in nature in **fossil wax** or **ozocerite**.

The products known as **vaseline**, petrolatum, (U. S.), **cosmoline**, etc., which are now so largely used in pharmacy and perfumery, are mixtures of paraffin and the heavier petroleum oils. Their consistency depends upon the relative proportion of the higher paraffins, of increasing fusing-point, which they contain, from the oily **petrolatum liquidum** (U. S.), to the hard **petrolatum durum** (U. S.). Like petroleum itself, its various commercial derivatives are not definite compounds, but mixtures of the hydrocarbons of this series.

## HALOID DERIVATIVES OF THE PARAFFINS.

By the action of Cl or Br upon the paraffins, or by the action of HCl, HBr or HI upon the corresponding hydroxids, compounds are obtained in which one of the H atoms of the hydrocarbon has been replaced by an atom of Cl, Br or I: $C_2H_6+Br_2=C_2H_5Br+HBr$, or $C_2H_5OH+HCl=C_2H_5Cl+H_2O$. These compounds may be considered as the chlorids, bromids or iodids of the alcoholic radicals, and are known as the **haloid ethers** or **haloid esters.**

When Cl is allowed to act upon $CH_4$, it replaces a further number of H atoms until finally carbon tetrachlorid, $CCl_4$, is produced. Considering marsh gas as **methyl hydrid**, $CH_3.H$, the first product of substitution is **methyl chlorid,** $CH_3Cl$; the second **monochlormethyl chlorid,** $CH_2Cl.Cl$; the third **dichlormethyl chlorid,** or chloroform, $CHCl_2.Cl$; and the fourth **carbon tetrachlorid,** $CCl_4$.

Similar derivatives are formed with Br and I, and with the other hydrocarbons of the series.

Nascent hydrogen reduces all of the halogen derivatives to the parent hydrocarbon: $CHCl_3+3H_2=CH_4+3HCl$.

Caustic potash or soda in alcoholic solution splits off the halogen and water, with formation of an unsaturated hydrocarbon: $CH_3.CH_2Br+KHO=CH_2:CH_2+KBr+H_2O$. Heated with aqueous potash the haloid esters produce the corresponding alcohols: $CH_3.CH_2Br+KHO=CH_3.CH_2OH+KBr$. Heated with alcoholic solution of potassium cyanid at 100°, the haloid esters produce the alkyl cyanids: $CH_3.CH_2I+KCN=CH_3.CH_2.CN+KI$. (p.340). They also combine with ammonia to form amins (p. 327): $CH_3Cl+NH_3=CH_3.NH_3.Cl$.

**Methyl Chlorid**—$CH_3Cl$—50.5—is a colorless gas, slightly soluble in $H_2O$, and having a sweetish taste and odor. It is prepared commercially by heating trimethylammonium chlorid (obtained by distilling beet sugar molasses): $3N(CH_3)_3HCl=2CH_3Cl+2N(CH_3)_3+NH_2CH_3+HCl$. It may be condensed to a liquid which boils at —22° (—7.6° F.), in which form it is used in ice machines, as a spray in neuralgia, and as an anæsthetic; for the latter uses either alone or mixed with $CHCl_3$,$C_4H_{10}O$, or $C_2H_5Cl$. It burns with a greenish flame.

**Dichlormethane—Methene chlorid—Methylene chlorid—Chloromethyl—Monochlormethyl chlorid**—$CH_2Cl_2$—85—is obtained by the action of Cl upon $CH_4$, and by the reduction of $CHCl_3$ by nascent hydrogen.

It is a colorless, oily liquid; boils at 40° (104° F.); sp. gr. 1.36; its odor is similar to that of chloroform; it is very slightly soluble in $H_2O$ and is not inflammable. It has been used as an anæsthetic, but has been discarded as being less safe than chloroform.

—Formyl chlorid—Dichlor-
ermum (U. S.; Br.)—$CHCl_3$
as still, 35–40 litres (9–11
ecently slacked lime and
s (4 qts.) of alcohol are
aised until the product
n. heat being again applied
ade chloroform so obtained is
hen by mixing with alcohol
ate, and distilling the mixture.
manufactured by the action of
reaction being expressed by the
$-2CHCl_3 + 2Ca(HO)_2 + (CH_3-$

ing chloral hydrate with an alkali:
$OK + H_2O$.
having a strong, agreeable, ether-
gr. 1.497; very sparingly soluble in
ther in all proportions; boils at
solvent for many substances insol-
rus, iodin, fats, resins, caoutchouc,

burns from a wick with a smoky, red
s not acted on by $H_2SO_4$, except after
en off. In direct sunlight Cl converts
alkalies in aqueous solution do not act
them in alcoholic solution, it is decom-
rid and formate of the alkaline metal.
not altered by exposure to light; but if it
ven in very minute quantity, it is gradu-
ction into HCl, Cl and other substances.
present in large amount, lowers the sp.
and causes it to fall through $H_2O$ in opaque,
in small amount it produces a green color
obtained by acting on ferrous chlorid with
nitrate and ammonium hydrosulfid). *Alde-*
olor when $CHCl_3$ containing it is heated with
*Chloric acid* reddens blue litmus, and causes a
aqueous solution of silver nitrate shaken with
*empyreumatic compounds* are the most dan-
s of chloroform. Their absence is recognized
acters: (1) When the chloroform is shaken with
olorless $H_2SO_4$, and allowed to stand 24 hours;
m) layer should be perfectly colorless, and the

lower (acid) layer colorless or faintly yellow. (2) When a small quantity is allowed to evaporate spontaneously, the last portions should have no pungent odor, and the remaining film of moisture should have no taste or odor other than those of chloroform.

**Analytical Characters.**—(1) Add a little alcoholic solution of potash and 2–3 drops of anilin and warm: the disagreeable odor of isobenzonitril (q. v.) is produced. (2) Vapor of $CHCl_3$, when passed through a red-hot tube, is decomposed with formation of HCl and Cl, the former of which is recognized by the production of a white ppt., soluble in ammonium hydroxid, in an acid solution of silver nitrate. This test does not afford reliable results when the substance tested contains a free acid and chlorids. (3) Dissolve about 0.01 gm. of $\beta$ naphthol in a small quantity of KHO solution, warm, and add the suspected liquid; a blue color is produced. (4) Add about 0.3 grm. resorcinol in solution, and 3 gtts. NaHO solution and boil strongly. In the presence of $CHCl_3$ a yellowish-red color is produced, and the liquid exhibits a beautiful yellow-green fluorescence.

**Toxicology.**—The action of chloroform varies as it is taken by the stomach or by inhalation. In the former case, owing to its insolubility, but little is absorbed, and the principal action is the local irritation of the mucous surfaces. Recovery has followed a dose of four ounces, and death has been caused by one drachm, taken into the stomach. Chloroform vapor acts much more energetically, and seems to owe its potency for evil to its paralyzing influence upon the respiratory nerve centers, and upon the cardiac ganglia. While persons suffering from heart disease are particularly susceptible to the paralyzing effect of chloroform vapor, there are many cases recorded of death from the inhalation of small quantities, properly diluted, in which no heart lesion was found upon a post-mortem examination. Chloroform is apparently not altered in the system, and is eliminated with the expired air.

No chemical antidote for chloroform is known. When it has been swallowed, stomach-lavage and emetics are indicated; when taken by inhalation, a free circulation of air should be established about the face; artificial respiration and the application of the induced current to the sides of the neck and epigastrium should be resorted to.

The nature of the poison is usually revealed at the autopsy by its peculiar odor, which is most noticeable on opening the cranial and thoracic cavities. In a toxicological analysis, chloroform is to be sought for especially in the lungs and blood. These are placed in a flask; if acid, neutralized with sodium carbonate, and subjected to distillation at the temperature of the water-bath. The vapors are passed through a tube of difficultly fusible glass; at first the tube is heated to redness for about an inch of its length, and test No. 2

applied to the issuing gas. The tube is then allowed to cool, and the distillate collected in a pointed tube, from the point of which any $CHCl_3$ is removed by a pipette and tested according to Nos. 1, 3 and 4 above.

**Carbon Tetrachlorid**—*Chlorocarbon*—$CCl_4$—154—is formed by the prolonged action, in sunlight, of Cl upon $CH_3Cl$ or $CHCl_3$; or more rapidly, by passing Cl, charged with the vapor of carbon disulfid, through a red-hot tube, and purifying the product.

It is a colorless, oily liquid, insoluble in $H_2O$; soluble in alcohol and in ether; sp. gr. 1.56; boils at 78° (172.4° F.). Its vapor is decomposed at a red heat into a mixture of the dichlorid, $C_2Cl_4$, trichlorid, $C_2Cl_6$, and free Cl.

**Methyl Bromid**—$CH_3Br$—95.—A colorless liquid; sp. gr. 1.664; boils at 13° (55.4° F.); formed by the combined action of P and Br on methyl hydroxid.

**Tribrommethane**—*Dibromomethyl bromid*—*Methenyl bromid*—*Formyl bromid*—**Bromoform**—$CHBr_3$.Br—253—is prepared by gradually adding Br to a cold solution of KHO in methyl alcohol until the liquid begins to be colored; and rectifying over $CaCl_2$.

A colorless, aromatic, sweet liquid; sp. gr. 2.13; boils at 150°–152° (302°–306° F.); solidifies at —9° (15.8° F.); sparingly soluble in $H_2O$; soluble in alcohol and ether. Boiled with alcoholic KHO it is decomposed in the same way as is $CHCl_3$.

Its physiological action is similar to that of $CHCl_3$. It occurs as an impurity of commercial Br, accompanied by **carbon tetrabromid**, $CBr_4$.

**Methyl Iodid**—$CH_3I$—142—a colorless liquid, sp. gr. 2.237; boils at 45° (113° F.); burns with difficulty, producing violet vapor of iodin. It is prepared by a process similar to that for obtaining the bromid, and is used in the anilin industry.

**Triiodomethane**—*Diiodomethyl iodid*—*Methenyl iodid*—*Formyl iodid*—**Iodoform**—**Iodoformum**, U. S.—$CHI_2I$—394.—Formed like $CHCl_3$ and $CHBr_3$, by the combined action of KHO and the halogen upon alcohol; it is also produced by the action of I upon a great number of organic substances, and is usually prepared by heating a mixture of alkaline carbonate, $H_2O$, I and ethylic alcohol, and purifying the product by recrystallization from alcohol. It is also produced from acetone by making a solution containing 50 gm. KI, 6 gm. acetone, and 2 gm. NaHO in 2 L. $H_2O$ and gradually adding a dilute solution of $KClO_3$.

Iodoform is a solid, crystallizing in yellow, hexagonal plates, which melt at 20° (248° F.). It may be sublimed, a portion being decomposed. It is insoluble in water, acids and alkaline solutions; soluble in alcohol, ether, carbon disulfid, and the fatty and essential

oils; the solutions, when exposed to the light, undergo decomposition and assume a violet-red color. It has a sweet taste, and a peculiar, penetrating odor, resembling, when the vapor is largely diluted with air, that of saffron. When heated with potash a portion is decomposed into formate and iodid, while another portion is carried off unaltered with the aqueous vapor. It contains 96.7% of its weight of iodin.

**Ethyl Chlorid**—*Hydrochloric or muriatic ether*—$C_2H_5Cl$—64.5.—A colorless, ethereal liquid; boils at 11° (51.8° F.); obtained by passing gaseous HCl through ethylic alcohol to saturation, and distilling over the water-bath. It is now used to produce cold by spraying. The liquid and vapor are readily inflammable.

By the continued action of Cl in the sunshine upon ethyl chlorid, or upon ethene chlorid, $C_2H_4,Cl_2$, a white, crystalline solid, **Hexachlorethane or carbon trichlorid,** $C_2Cl_6$, is produced. It is insoluble in $H_2O$, soluble in alcohol and in ether, has an aromatic odor, fuses at 160° (320° F.), and boils at 182° (359.6° F.).

**Ethyl Bromid**—*Hydrobromic ether*—$C_2H_5Br$—109—A colorless, ethereal liquid; boils at 40.7° (105.3° F.) obtained by the combined action of P and Br on ethylic alcohol. It is now extensively used as an anæsthetic in minor surgery.

**Ethyl Iodid**—*Hydriodic ether*—$C_2H_5I$—156—is prepared by placing absolute alcohol and P in a vessel surrounded by a freezing mixture and gradually adding I. When the action has ceased, the liquid is decanted, distilled over the water-bath and the distillate washed and rectified.

It is a colorless liquid; boils at 72.2° (162° F.); has a powerful, ethereal odor; burns with difficulty. It is largely used in the anilin industry.

[See also Esters of Glycols, p. 315.]

## OXIDATION PRODUCTS OF THE PARAFFINS.

Five important and distinct classes of compounds are derivable from the saturated hydrocarbons by oxidation:

One of these may be considered as derived from the hydrocarbon by the insertion of an oxygen atom between two of its hydrocarbon groups. Thus from the hydrocarbon $CH_3.CH_2.CH_2.CH_3$ we may derive the oxids $CH_3.O.CH_2.CH_2.CH_3$, and $CH_3.CH_2.O.CH_2.CH_3$. These are the true oxids of the hydrocarbon radicals, and are known as the **simple ethers.** It will be more convenient to consider them after having discussed the other oxidation products.

The other four classes are more closely related to each other.

They may be considered as being derived from the hydrocarbons in one of two ways; either

(1) By the interpolation or substitution, or both, of an oxygen atom or atoms in one of the groups $CH_3$, $CH_2$, or CH of the parent hydrocarbon (see formulæ on p. 230). Thus:

$(H_2{:}C.H)'$ becomes $(H_2{:}C.O.H)'$; $(O{:}C.H)'$ or $(O{:}C.O.H)'$
$(H.C.H)''$ " $(H.C.O.H)''$ or $(C{:}O)''$ and
$(C.H)'''$ " $(C.O.H)'''$

and by the oxidation of a single group in the hydrocarbon: isopentane; $(CH_3)_2{:}CH.CH_2.CH_3$ the following products may be obtained:

| | | | | | |
|---|---|---|---|---|---|
| $(CH_3)_2$ ‖ CH \| $CH_2$ \| $H_2{:}C.O.H$ | $(CH_3)_2$ ‖ CH \| $CH_2$ \| $O{:}C.H$ | $(CH_3)_2$ ‖ CH \| $CH_2$ \| $O{:}C.O.H$ | $(CH_3)_2$ ‖ CH \| $H.C.O.H$ \| $CH_3$ | $(CH_3)_2$ ‖ CH \| $C{:}O$ \| $CH_3$ | $(CH_3)_2$ ‖ $C.O.H$ \| $CH_2$ \| $CH_3$ |
| *Primary Alcohol.* | *Aldehyde.* | *Acid.* | *Secondary Alcohol.* | *Ketone.* | *Tertiary Alcohol.* |
| Isobutyl Carbinol. | Valeraldehyde. | Isovalerianic Acid. | Methyl isopropyl Carbinol. | Methyl isopropyl Ketone. | Dimethyl ethyl Carbinol. |

(2) Or these compounds may be considered as produced by the substitution of hydroxyls (OH), for one or more of the hydrogen atoms of the hydrocarbon, it being remembered that when a substance is thus produced in which two hydroxyls are attached to the same carbon atom, water separates, except under the circumstances referred to on page 225. Thus from the hydrocarbon: propane, $CH_3.CH_2.CH_3$, the following products may be derived by substitution in a single hydrocarbon group:

$CH_3.CH_2.C\langle{}^{H_2}_{OH}$ = Primary alcohol;

$CH_3.CH_2.C\langle{}^{H}_{(OH)_2} - H_2O = CH_3.CH_2.C\langle{}^{H}_{O}$ = Aldehyde;

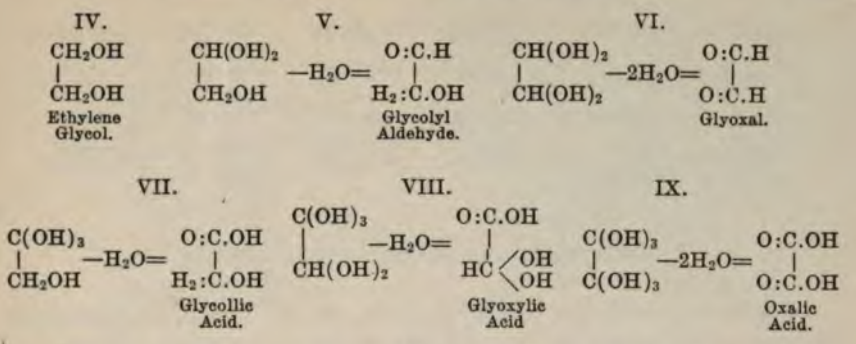
$CH_3.CH_2.C{:}(OH)_3 - H_2O = CH_3.CH_2.C\langle{}^{OH}_{O}$ = Acid;

$CH_3.(CH.OH).CH_3$ = Secondary alcohol;

$CH_3.(C{:}[OH]_2).CH_3 - H_2O = CH_3.(C{:}O).CH_3$ = Ketone.

When the number of hydroxyls substituted in each hydrocarbon group exceeds one, the number of derivatives increases rapidly with an increasing number of C atoms in the parent hydrocarbon. Thus the second term of the series, $CH_3.CH_3$, yields nine derivatives (p. 225):

| I. | II. | III. |
|---|---|---|
| $CH_2OH$ \| $CH_3$ | $CH(OH)_2$ \| $CH_3$ $-H_2O=$ $O{:}C.H$ \| $CH_3$ | $C(OH)_3$ \| $CH_3$ $-H_2O=$ $O{:}C.OH$ \| $CH_3$ |
| Ethylic Alcohol. | Acetic Aldehyde. | Acetic Acid. |




There are twenty-nine possible derivatives of the third hydrocarbon, $CH_3.CH_2.CH_3$.

The four classes of oxidation products under consideration are therefore :

**A. The alcohols,** subdivided into (*a*) *Primary*, containing the group $-C\langle^{H_2}_{OH}$; (*b*) *Secondary*, containing the group $=C\langle^{H}_{OH}$; and (*c*) *Tertiary*, containing the group $\equiv C.OH$;

**B. The aldehydes,** containing the group $-C\langle^{O}_{H}$;

**C. The ketones,** containing the group $=C=O$; and

**D. The carboxylic acids,** containing the group **carboxyl**: $-C\langle^{O}_{OH}$.

## ALCOHOLS—HYDROCARBON HYDROXIDS.

These substances are mainly characterized by their power of entering into double decomposition with acids to form neutral compounds, called **esters,** water being at the same time formed at the expense of both alcohol and acid. **They are the hydroxids of hydrocarbon radicals, the alkyls, and as such resemble the metallic hydroxids, while the esters are the counterparts of the metallic salts :**

$$\left.\begin{matrix}(C_2H_5)\\H\end{matrix}\right\}O + \left.\begin{matrix}(C_2H_3O)\\H\end{matrix}\right\}O = \left.\begin{matrix}(C_2H_3O)\\(C_2H_5)\end{matrix}\right\}O + \left.\begin{matrix}H\\H\end{matrix}\right\}O$$

Ethyl hydroxid. Acetic acid. Ethyl acetate. Water.

$$\left.\begin{matrix}K\\H\end{matrix}\right\}O + \left.\begin{matrix}(C_2H_3O)\\H\end{matrix}\right\}O = \left.\begin{matrix}(C_2H_3O)\\K\end{matrix}\right\}O + \left.\begin{matrix}H\\H\end{matrix}\right\}O$$

Potassium hydroxid. Acetic acid. Potassium acetate. Water.

Or they may be regarded as substances derived from the hydrocarbons by the substitution of one or more hydroxyls for one or more hydrogen atoms. Alcohols containing one OH are designated as **monoatomic** or **monohydric**; those containing two OH groups are **diatomic or dihydric,** etc.:

| $CH_2OH$ | $CH_2OH$ | $CH_2OH$ | $CH_2OH$ | $CH_2OH$ | $CH_2OH$ |
|---|---|---|---|---|---|
| \| | \| | \| | \| | \| | \| |
| $CH_2$ | $CH_2$ | CHOH | $(CHOH)_2$ | $(CHOH)_3$ | $(CHOH)_4$ |
| \| | \| | \| | \| | \| | \| |
| $CH_3$ | $CH_2OH$ | $CH_2OH$ | $CH_2OH$ | $CH_2OH$ | $CH_2OH$ |
| Ethylic Alcohol, Monoatomic. | Propyl Glycol, Diatomic. | Glycerol, Triatomic. | Erythrol, Tetratomic. | Arabite, Pentatomic. | Mannitol, Hexatomic. |

## MONOATOMIC, OR MONOHYDRIC ALCOHOLS.

Beginning with the third member of the series, an increasing number of isomeres of the higher terms are known. These are divided into three classes:

I. Some of these alcohols yield on oxidation, first, an aldehyde containing the group $(CHO)'$ and then an acid containing the group $(COOH)'$, both aldehyde and acid containing the same number of carbon atoms as the alcohol. These alcohols contain the characterizing group $(CH_2OH)'$, and are called **primary alcohols**, e. g., ethylic alcohol: $CH_3.CH_2OH$.

II. Other monoatomic alcohols yield on oxidation, not an aldehyde or an acid, but a ketone, containing the group $(CO)''$ and the same number of carbon atoms as the alcohol. These alcohols contain the characterizing group $(CHOH)''$, and are called **secondary alcohols, or isoalcohols**, e. g., Isopropyl alcohol: $CH_3.CHOH.CH_3$.

III. Still other alcohols yield on oxidation no product containing the same number of carbon atoms as the alcohol, but either two or more acids, or an acid and a ketone, whose molecules contain a less number of carbon atoms than the alcohol from which they were derived. These alcohols contain the characterizing group $(COH)'''$, and are called **tertiary alcohols**, e. g., Tertiary butyl alcohol, $(CH_3)_3$: COH.

**Nomenclature.**—Names of alcohols terminate in *ol;* and the termination *ol* is reserved for the names of alcohols and of phenols. The "Geneva" names of the monohydric alcohols are derived from those of the corresponding hydrocarbons by the substitution of the syllable *ol* for the terminal *e*: Thus $H.CH_2OH$ is Methanol; $CH_3.CH_2$-OH ethanol; $CH_3.CH_2.CH_2OH$,1-propanol; $CH_3.CHOH.CH_3$,2-propanol, etc.

Kolbe's system of naming the monoatomic alcohols is more generally followed. It refers the names of the higher alcohols back to that of the first, $H.CH_2OH$, which is called **carbinol**; the names of the radicals contained in the superior homologues being prefixed to the word "*carbinol*" in the construction of their names. Thus the graphic formulæ and carbinol names of the eight possible amylic alcohols are as follows:

*Primary.*

(1) $CH_3.CH_2.CH_2.CH_2.CH_2OH$
Butyl Carbinol.
(Normal amylic alcohol.)

(2) $\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!CH.CH_2.CH_2OH$
Isobutyl Carbinol.
(Amylic alcohol of fermentation.)

(3) $\begin{matrix}CH_3\\CH_3.CH_2\end{matrix}\!\!>\!CH.CH_2OH$
Secondary butyl Carbinol.
(Active amylic alcohol).

(4) $\begin{matrix}CH_3\\CH_3—C.CH_2OH\\CH_3\end{matrix}$
Tertiary butyl Carbinol.

*Secondary.*

(5) $\begin{matrix}CH_3.CH_2\\CH_3.CH_2\end{matrix}\!\!>\!CHOH$
Diethyl Carbinol.

(6) $\begin{matrix}CH_3\\CH_3.CH_2.CH_2\end{matrix}\!\!>\!CHOH$
Methyl n-propyl Carbinol.

(7) $\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!CH\!<\!\begin{matrix}CH_3\\CH_3\end{matrix}$
Methyl isopropyl Carbinol.

*Tertiary.*

(8) $\begin{matrix}CH_3\\CH_3—C.OH\\CH_3.CH_2\end{matrix}$
Dimethyl ethyl Carbinol.

Of the above, numbers 1, 5 and 6 are derived from the normal paraffin (1, page 230); numbers 2, 3, 7 and 8 from the isoparaffin (2), and number 4 from the mesoparaffin (3).

**General Methods of Formation.**—(1) By the action of freshly precipitated, moist silver hydroxid upon the haloid esters: $C_2H_5I+AgHO=C_2H_5OH+AgI$.

(2) By the saponification of their esters by caustic potash: $C_2H_3O_2.C_2H_5+KHO=C_2H_5.OH+C_2H_3O_2K$.

(3) Primary alcohols are produced by the reduction of aldehydes, acid chlorids, or anhydrids (pp. 256, 311, 310): $C_2H_5.CHO+H_2=C_2H_5.CH_2OH$, or $C_2H_5.COCl+2H_2=C_2H_5.CH_2OH+HCl$, or $(CH_3CO)_2O+2H_2=CH_3.CH_2OH+CH_3.COOH$.

(4) By the action of nitrous acid upon the primary amins (p. 328); $CH_3.CH_2.NH_2+HNO_2=CH_3.CH_2OH+N_2+H_2O$.

(5) Secondary alcohols are formed by the reduction of ketones: $CH_3.CO.CH_3+H_2=CH_3.CHOH.CH_3$.

**Methyl Hydroxid—Carbinol—Pyroxylic spirit—Methylic alcohol—Wood spirit**—$H.CH_2OH=32$—may be formed from marsh-gas, $CH_3H$, by first converting it into the iodid, and acting upon this with potassium hydroxid: $CH_3I+KHO=KI+H.CH_2OH$. It is usually obtained by the destructive distillation of wood. The **crude wood vinegar** so produced is a mixture of acetic acid and methyl alcohol with a variety of other products. The crude vinegar, separated from tarry products, is redistilled; the first tenth of the distillate is treated with quicklime and again distilled; the distillate treated with dilute $H_2SO_4$: decanted and again distilled. The product, still quite impure, is the **wood alcohol, wood naphtha,** or **pyroxylic spirit** of commerce. The pure hydroxid can only be obtained by decomposing a crystalline compound, such as methyl oxalate, and rectifying the product until the boiling-point is constant at 66.5° (151.7° F.).

Pure methyl alcohol is a colorless liquid, having an ethereal and

alcoholic odor, and a sharp, burning taste; sp. gr. 0.814 at 0°; boils at 66.5° (151.7° F.); burns with a pale flame, giving less heat than that of ethylic alcohol; mixes with water, alcohol, and ether in all proportions; is a good solvent of resinous substances, and also dissolves sulfur, phosphorus, potash, and soda.

Methyl hydroxid is not affected by exposure to air under ordinary circumstances, but in the presence of platinum-black it is oxidized, with formation of the corresponding aldehyde, formaldehyde, and acid, formic acid. Hot $HNO_3$ decomposes it with formation of nitrous fumes, formic acid and methyl nitrate. It is acted upon by $H_2SO_4$ in the same way as ethyl alcohol. The organic acids form methyl esters with it. With HCl under the influence of a galvanic current, it forms an oily substance having the composition $C_2H_3OCl$.

**Methylated spirit** is ethyl alcohol containing one-ninth its volume of wood spirit.

**Ethyl Hydroxid—Ethylic alcohol—Methyl carbinol—*Vinic alcohol*—Alcohol—Spirits of wine**—$CH_3.CH_2OH$—46.

**Preparation.**—Industrially alcohol and alcoholic liquids are obtained from substances rich in starch or glucose.

The manufacture of alcohol consists of three distinct processes: (1) the conversion of starch into sugar; (2) the fermentation of the saccharine liquid; (3) the separation, by distillation, of the alcohol formed by fermentation.

The raw materials for the first process are **malt** and some substance (grain, potatoes, rice, corn, etc.) containing starch. Malt is barley which has been allowed to germinate, and, at the proper stage of germination, roasted. During this growth there is developed in the barley a peculiar nitrogenous principle called **diastase.** The starchy material is mixed with a suitable quantity of malt and water, and the mass maintained at a temperature of 65°–70° (149°–158° F.) for two to three hours, during which the diastase rapidly converts the starch into **dextrin**, and this in turn into **maltose** and **glucose.**

The saccharine fluid, or **wort**, obtained in the first process, is drawn off, cooled, and **yeast** is added. As a result of the growth of the yeast-plant, a complicated series of chemical changes take place, the principal one of which is the splitting up of the glucose into carbon dioxid and alcohol: $C_6H_{12}O_6=2C_2H_5OH+2CO_2$. There are formed at the same time small quantities of glycerol, succinic acid, and propylic, butylic, and amylic alcohols.

An aqueous fluid is thus obtained which contains 3–15 per cent of alcohol. This is then separated by the third process, that of distillation and rectification. The apparatus used for this purpose has

been so far perfected that by a single distillation an alcohol of 90–95 per cent. can be obtained.

In some cases alcohol is prepared from fluids rich in glucose, such as grape juice, molasses, syrup, etc. In such cases the first process becomes unnecessary.

Commercial alcohol always contains $H_2O$, and when pure or *absolute* alcohol is required, the commercial product must be mixed with some hygroscopic solid substance, such as quicklime, from which it is distilled after having remained in contact twenty-four hours.

**Fermentation.**—This term (derived from *fervere* = to boil) was originally applied to alcoholic fermentation, by reason of the bubbling of the saccharine liquid caused by the escape of $CO_2$; subsequently it came to be applied to all decompositions similarly attended by the escape of gas.

At present it is used by many authors to apply to a number of heterogeneous processes; and some writers distinguish between "true" and "false" fermentation. It is best, we believe, to limit the application of the term to those decompositions designated as *true fermentations*.

**Fermentation is a decomposition of an organic substance, produced by the processes of nutrition of a low form of animal or vegetable life.**

The **true ferments** are therefore all organized beings, such as *torula cerevisiæ*, producing alcoholic fermentation; *penicillium glaucum*, producing lactic acid fermentation; and *mycoderma aceti*, producing acetic acid fermentation.

The false fermentations are not produced by an organized body, but by a soluble, unorganized, nitrogenous substance, whose method of action is as yet imperfectly understood. The unorganized ferments, such as diastase, pepsin, etc., are called **enzymes.**

An interesting total synthesis of alcohol is from calcium carbid, water and hydrogen. Acetylene is formed by the action of water upon calcium carbid, $CaC_2 + 2H_2O = CaH_2O_2 + C_2H_2$; vapors of acetylene and water, heated together to 325° (617° F.) unite to form aldehyde, $C_2H_2 + H_2O = CHO.CH_3$; and nascent hydrogen converts aldehyde into alcohol, $CHO.CH_3 + H_2 = CH_2OH.CH_3$.

**Properties.**—Alcohol is a thin, colorless, transparent liquid, having a spirituous odor and a sharp, burning taste; sp. gr. 0.8095 at 0°, 0.7939 at 15° (59° F.); it boils at 78.5° (173.3° F.), and solidifies at —130.5° (—202.9° F.). At temperatures below —90° (—130° F.) it is viscous. It mixes with water in all proportions, the union being attended by elevation in temperature and contraction in volume (after cooling to the original temperature). It also attracts moisture

from the air to such a degree that absolute alcohol only remains such for a very short time after its preparation. It is to this power of attracting $H_2O$ that alcohol owes its preservative power for animal substances. It is a very useful solvent, dissolving a number of gases, many mineral and organic acids and alkalies, most of the chlorids and carbonates, some of the nitrates, and the essences and resins. The sulfates are insoluble in alcohol. Alcoholic solutions of fixed medicinal substances are called **tinctures**; those of volatile principles, **spirits.**

The action of oxygen upon alcohol varies according to the conditions. Under the influence of energetic oxidants, such as chromic acid, or, when alcohol is burned in the air, the oxidation is rapid and complete, and is attended by the extrication of much heat, and the formation of carbon dioxid and water: $C_2H_6O+3O_2=2CO_2+3H_2O$. Mixtures of air and vapor of alcohol explode upon contact with flame. If a less active oxidant be used, such as platinum-black, or by the action of atmospheric oxygen at low temperatures, a simple oxidation of the alcoholic radical takes place, with formation of *acetic acid:* $CH_3.CH_2OH + O_2 = CH_3.COOH+H_2O$, a reaction which is utilized in the manufacture of acetic acid and vinegar. If the oxidation be still further limited, *aldehyde* is formed: $2CH_3.CH_2OH + O_2=2CH_3.CHO+2H_2O$. If vapor of alcohol be passed through a tube filled with platinum sponge and heated to redness, or if a coil of heated platinum wire be introduced into an atmosphere of alcohol vapor, the products of oxidation are quite numerous: among them are water, ethylene, aldehyde, acetylene, carbon monoxid, and acetal. Heated platinum wire introduced into vapor of alcohol continues to glow by the heat resulting from the oxidation, a fact which has been utilized in the thermocautery.

Chlorin and bromin act energetically upon alcohol, producing a number of chlorinated and brominated derivatives, the final products being *chloral* and *bromal* (p. 258). If the action of Cl be moderated, aldehyde and HCl are first produced. Iodin acts quite slowly in the cold, but old solutions of I in alcohol (Tr. iodin.) are found to contain HI, ethyl iodid, and other imperfectly studied products. In the presence of an alkali, I acts upon alcohol to produce iodoform. Potassium and sodium dissolve in alcohol with evolution of H; upon cooling, a white solid crystallizes, which is the double oxid of ethyl and the alkali metal, and is known as potassium or sodium **ethylate** or **alcoholate.** Nitric acid, aided by a gentle heat, acts violently upon alcohol, producing nitrous ether, brown fumes, and products of oxidation. (For the action of other acids upon alcohol see the corresponding esters and the ethers.) The hydroxids of the alkali metals dissolve in alcohol, but react upon it slowly; the solution turns

brown and contains an acetate. If alcohol be gently heated with $HNO_3$ and nitrate of silver or of mercury, a gray precipitate falls, which is silver or mercury fulminate.

**Varieties.**—It occurs in different degrees of concentration: **absolute alcohol** is pure alcohol, $C_2H_6O$. It is not purchasable, and must be made as required. The so-called absolute alcohol of the shops is rarely stronger than 98 per cent. **Alcohol** (U. S.), sp. gr. 0.820, contains 94 per cent. by volume, and **spiritus rectificatus** (Br.), sp. gr. 0.838, contains 84 per cent. This is the ordinary rectified spirit used in the arts. **Alcohol dilutum** (U. S.)=**Spiritus tenuior** (Br.), sp. gr. 0.920, used in the preparation of tinctures, contains 53 per cent. It is of about the same strength as the **proof spirit** of commerce.

**Analytical Characters.**—(1) Heated with a small quantity of solution of potassium dichromate and $H_2SO_4$, the liquid assumes an emerald-green color, and, if the quantity of $C_2H_6O$ be not very small, the peculiar fruity odor of aldehyde is developed. (2) Warmed and treated with a few drops of potash solution and a small quantity of iodin, an alcoholic liquid deposits a yellow, crystalline ppt. of iodoform, either immediately or after a time. (3) If $HNO_3$ be added to a liquid containing $C_2H_6O$, nitrous ether, recognizable by its odor, is given off. If a solution of mercurous nitrate with excess of $HNO_3$ be then added, and the mixture heated, a further evolution of nitrous ether occurs, and a yellow-gray deposit of fulminating mercury is formed, which may be collected, washed, dried, and exploded. (4) If an alcoholic liquid be heated for a few moments with $H_2SO_4$ diluted with $H_2O$ and distilled, the distillate, on treatment with $H_2SO_4$ and potassium permanganate, and afterward with sodium thiosulfate, yields aldehyde, which may be recognized by the production of a violet color with a dilute solution of fuchsin.

None of the above reactions, *taken singly*, is characteristic of alcohol.

Alcohol is determined quantitatively in simple mixtures of alcohol and water by determining the specific gravity and referring to tables constructed for the purpose. In alcoholic beverages 100 cc. of the sample is distilled until 75 cc. have passed over, the distillate is then made up to 100 cc. with water, and the sp. gr. determined.

**Alcoholic Beverages.**—These may be divided into four classes:

I.—Those prepared by the fermentation of malted grain—**beers, ales** and **porters.**

II.—Those prepared by the fermentation of grape juice—**wines.**

III.—Those prepared by the fermentation of the juices of fruits other than the grape—**cider, fruit-wines.**

IV.—Those prepared by the distillation of some fermented saccharine liquid—**ardent spirits.**

**Beer**, ale and porter are aqueous infusions or decoctions of malted grain, fermented and flavored with hops. They contain, therefore, the soluble constituents of the grain employed; dextrin, maltose and glucose, produced during the malting; alcohol and carbon dioxid, produced during the fermentation; and the soluble constituents of the flavoring material. The alcoholic strength of malt liquors varies from 1.5 to 9 per cent. absolute alcohol by weight. Weiss-beer contains 1.5–1.9 per cent.; lager, 4.1–4.5 per cent.; bock-beer, 3.88–5.23 per cent.; London porter, 5.4–6.9 per cent.; Burton ale, 5.9 per cent.; Scotch ale, 8.5–9 per cent. Malt liquors all contain a considerable quantity of nitrogenous material (0.4–1 per cent. N), and succinic, lactic and acetic acids. The amount of inorganic material, in which the phosphates of potassium, sodium and magnesium predominate largely, varies from 0.2 to 0.3 per cent. The sp. gr. is from 1.014 to 1.033.

The adulterations of malt liquors are numerous and varied. Sodium carbonate is added with the double purpose of neutralizing an excess of acetic acid and increasing the foam. The most serious adulteration consists in the use of artificial glucose as a substitute for malt, and, more rarely, in the introduction of bitter principles other than hops, and notably of strychnin, cocculus indicus (picrotoxin), and picric acid.

**Wines** are produced by the fermentation of grape juice. In the case of red wines the **marc**, or mass of skins, seed and stems, is allowed to remain in contact with the **must**, or fermenting juice, until, by production of alcohol, the liquid dissolves a portion of the coloring matter of the skins. A certain proportion of tannin is also dissolved, whose presence is necessary to prevent *stringiness*. Sweet wines are produced from must rich in glucose, and by arresting the fermentation before that sugar has been completely decomposed. Dry wines are obtained by more complete fermentation of must less rich in glucose. Tartaric acid is the predominating acid in grape juice, and, as the proportion of alcohol increases during fermentation, the acid potassium tartrate is deposited.

Most wines of good quality improve in flavor with age, and this improvement is greatly hastened by the process of **pasteuring**, which consists in warming the wine to a temperature of 60° C. (140° F.), without contact of air.

**Light wines** are those whose percentage of alcohol is less than 12 per cent. In this class are included the clarets, Sauternes, Rhine and Moselle wines; champagnes, Burgundies, the American wines (except some varieties of California wine), Australian, Greek, Hungarian and Italian wines.

The champagnes and some Moselle wines are sparkling, a quality

which is communicated to them by carbon dioxid produced by a secondary fermentation set up in the bottled wine, and held in solution by its own pressure.

Of the still wines the most widely used are the *clarets*, **Vinum rubrum** (U. S.), or red Bordeaux wines, and the *hocks*, **Vinum album** (U. S), or white Rhine, Moselle and American wines. The former are of low alcoholic strength, mildly astringent, and contain but a small quantity of nitrogenous material. The Rhine wines are thinner and more acid, and generally of lower alcoholic strength than the clarets. The Burgundy and Rhone wines are celebrated for their high flavor and body; they are not strongly alcoholic, but contain a large quantity of nitrogenous material. Our native American wines, particularly those of the Ohio valley and of California, are yearly improving in flavor and quality. They more closely resemble the Rhine wines, clarets and Sauternes than other European wines.

**Heavy wines** are those whose alcoholic strength is greater than 12 per cent., usually 14 to 25 per cent.; they include the sherries, ports, Madeiras, Marsala, and some California wines, and are all the products of warm climates. Sherry is an amber-colored wine, grown in the south of Spain, **Vinum Xericum** (Br.); Marsala closely resembles sherry in appearance, and is frequently substituted for it. Port is a rich, dark-red wine, grown in Portugal.

The adulteration of wine by the addition of *foreign* substances is confined almost entirely to their artificial coloration, which is produced by the most varied substances, indigo, logwood, fuchsin, etc. The addition of natural constituents of wines, obtained from other sources, and the mixing of different grades of wine are, however, extensively practiced. Water and alcohol are the chief substances so added; and excess of the former may be detected by the taste and the low sp. gr. after expulsion of the alcohol. Most wines intended for export are **fortified** by the addition of alcohol. When the alcoholic spirit used is free from amyl alcohol, and is added in moderate quantities, there can be no serious objection to the practice, especially when applied to certain wines which, without such treatment, do not bear transportation. The mixing of fine grades of wine with those of a poorer quality is extensively practiced, particularly with sherries, champagnes, clarets and Burgundies, and is perfectly legitimate. The same cannot be said, however, of the manufacture of factitious wine, either entirely from materials not produced from the grape, or by converting white into red wines, or by mixing wines with coloring matters, alcohol, etc., to produce imitations of wines of a different class, an industry which flourishes extensively in Normandy, at Bingen on the Rhine, and at Hamburg. The wines so produced are usually heavy wines, port and sherry, so called.

**Cider** is the fermented juice of the apple, prepared very much in the same way as wine is from grape juice, and containing from 3.5 to 7.5 per cent. of alcohol. It is very prone to acetous fermentation, which renders it sour and not only unpalatable but liable to produce colic and diarrhœa with those not hardened to its use.

**Spirits** are alcoholic beverages, prepared by fermentation and distillation. They differ from beers and wines in containing a greater proportion of alcohol (35 to 50 per cent.), and in not containing any of the non-volatile constituents of the grains or fruits from which they are prepared. Besides alcohol and water they contain acetic, butyric, valerianic and œnanthic esters, to which they owe their flavor; sometimes tannin and coloring matter derived from the cask; amylic and other higher alcohols; sugar intentionally added, and caramel.

The varieties of spirituous beverages in common use are: **Brandy, spiritus vini gallici** (U. S., Br.), obtained by the distillation of wine, and manufactured in France and in California and Ohio. It is of sp. gr. 0.929 to 0.934, is dark or light in color, according to the quantity of burnt sugar added, and contains about 1.2 per cent. of solid matter. **American whisky, spiritus frumenti** (U. S.), prepared from wheat, rye, barley, or Indian corn; has a sp. gr. of 0.922 to 0.937 and contains 0.1 to 0.3 per cent. of solids. **Scotch and Irish whiskies**, colorless spirits distilled from fermented grains; sp. gr. 0.915 to 0.920, having a peculiar smoky flavor produced by drying the malted grain by a peat fire. **Gin**, also distilled from malted grain, sp. gr. 0.930 to 0.944, flavored with juniper, and sometimes fraudulently with turpentine. **Rum**, a spirit distilled from molasses, and varying in color and flavor from the dark *Jamaica rum* to the colorless *St. Croix rum*. The former is of sp. gr. 0.914 to 0.926, and contains one per cent. of solid matter. Brandy, whisky, etc., owe their color to a pigment formed by charring the interior of the white-oak casks.

**Liqueurs** or **cordials** are spirits sweetened and flavored with vegetable aromatics, and frequently colored; *anisette* is flavored with aniseed; *absinthe*, with wormwood; *curaçoa*, with orange peel; *kirschwasser*, with cherries, the stones being cracked and the spirits distilled from the bruised fermented fruit; *kümmel*, with cummin and caraway seeds; *maraschino*, with cherries; *noyau*, with peach and apricot kernels.

**Propyl Hydroxid—Ethyl carbinol—Primary propyl alcohol—** $CH_3.CH_2.CH_2OH$—60—is produced, along with ethylic alcohol, during fermentation, and obtained by fractional distillation of marc brandy, from *cognac oil*, *huile de marc* (not to be confounded with oil of wine), an oily matter, possessing the flavor of inferior brandy, which separates from marc brandy, distilled at high temperatures;

and from the residues of manufacture of alcohol from beet-root, grain, molasses, etc. It is a colorless liquid, has a hot alcoholic taste, and a fruity odor; boils at 96.7° (206.1° F.); and is miscible with water. It has not been put to any use in the arts. Its intoxicating and poisonous actions are greater than those of ethyl alcohol It exists in small quantity in cider.

**Butyl Alcohols**—$C_4H_9OH$—74.—The four butyl alcohols theoretically possible are known to exist:

**Propyl Carbinol—Primary normal butyl alcohol**—*Butyl alcohol of fermentation*—$CH_3.CH_2.CH_2.CH_2OH$—is formed in small quantities during alcoholic fermentation, and may be obtained by repeated fractional distillation from the oily liquid left in the rectification of vinic alcohol. It is a colorless liquid; boils at 116.8° (245.8° F.). It is more actively poisonous than ethyl or methyl alcohol.

**Isopropyl Carbinol—Isobutyl alcohol**—$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!CH.CH_2OH$—occurs in the fusel oil obtained in the products of fermentation and distillation of beet-root molasses. It is a colorless liquid, sp. gr 0.8032; boils at 108.4° (219.1° F.).

**Ethyl-methyl Carbinol—Secondary butyl alcohol**—*Butylene hydrate*—$\begin{matrix}CH_3—CH_2\\CH_3\end{matrix}\!\!>\!CHOH$—a liquid which boils at 99° (210.2° F.).

**Trimethyl Carbinol—Tertiary butyl alcohol**, $\begin{matrix}CH_3\\CH_3—C—OH\\CH_3\end{matrix}$—a crystalline solid which fuses at 25° (77° F.), and boils at 82° (179.6° F.).

**Amylic Alcohols**—$C_5H_{11}OH$—88.—The eight amyl alcohols theoretically possible (see p. 241) are known. The substance usually known as **amylic alcohol, potato spirit, fusel oil, alcohol amylicum** (Br.), is the primary alcohol, $\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!CH.CH_2.CH_2OH$, with lesser quantities of other alcohols, differing in nature and amount with the grain used, and the conditions of the fermentation and distillation, each kind of "spirit" furnishing and containing a peculiar fusel.

In the process of manufacture of ardent spirits the fusel oil accumulates in great part in the still, but much of it distils over, and is more or less completely removed from the product by the process of **defuselation.**

Spirits properly freed of fusel oil give off no irritating or foul fumes when hot. They are not colored red when mixed with three parts $C_2H_6O$ and one part strong $H_2SO_4$. They are not colored red or black by ammoniacal silver nitrate solution. When 150 parts of the spirit, mixed with 1 part potash, dissolved in a little $H_2O$, are evaporated down to 15 parts, and mixed with an equal volume of dilute $H_2SO_4$, no offensive odor should be given off.

While young spirits owe their rough taste, and, in great measure, their intoxicating qualities to the presence of fusel oil, it is a popular

error that a whisky would be improved by complete removal of all products except ethyl alcohol. The improvement of a spirit by age is due to chemical changes in the small amount of fusel retained in a properly manufactured product, and, were this absent, the spirit would deteriorate rather than improve by age.

The individual amylic alcohols have the following characters: **Butyl carbinol; normal amylic alcohol,**—$CH_3.CH_2.CH_2.CH_2.CH_2OH$—is a colorless liquid, boils at 137° (278.6° F.). Obtained from normal butyl alcohol, or from normal amylamin. It yields normal valerianic acid on oxidation.

**Isobutyl Carbinol—Amyl alcohol**—$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!CH.CH_2.CH_2OH$—is the principal constituent of the fusel oil from grain and potatoes. It is obtained from the last milky products of rectification of alcoholic liquids. These are shaken with $H_2O$ to remove ethyl alcohol, the supernatant oily fluid is decanted, dried by contact with fused calcium chlorid, and distilled; that portion which passes over between 128° and 132° (262.4°–269.6° F.) being collected.

It is a colorless, oily liquid, has an acrid taste and a peculiar odor, at first not unpleasant, afterward nauseating and provocative of severe headache. It boils at 131.4° (236.5° F.), and crystallizes at —20° (4° F.); sp. gr. 0.8184 at 15° (5° F.). It mixes with alcohol and ether, but not with water. It burns with a pale blue flame when sufficiently heated.

When exposed to air it oxidizes very slowly; quite rapidly, however, in contact with platinum-black, forming isovalerianic acid. The same acid, along with other substances, is produced by the action of the more powerful oxidants upon amyl alcohol. Chlorin attacks it energetically, forming amyl chlorid, HCl, and other chlorinated derivatives. Sulfuric acid dissolves in amyl alcohol, with formation of amyl-sulfuric acid, $SO_4(C_5H_{11})H$, corresponding to ethyl-sulfuric acid (p. 312). It also forms similar acids with phosphoric, oxalic, citric, and tartaric acids. Its esters, when dissolved in ethyl alcohol, have the taste and odor of various fruits, and are used in the preparation of artificial fruit-essences. Amyl alcohol is also used in analysis as a solvent, particularly for certain alkaloids, and in pharmacy for the artificial production of valerianic acid and the valerianates.

**Diethyl Carbinol**—$\begin{matrix}CH_3—CH_2\\CH_3—CH_2\end{matrix}\!\!>\!CHOH$—is produced by the action of a mixture of zinc and ethyl iodid on ethyl formate, with the subsequent addition of $H_2O$. It is a liquid which boils at 116.5° (241.7° F.).

**Methyl-propyl Carbinol**—$CH_3—CH_2—\begin{matrix}CH_3\\CH_2\end{matrix}\!\!>\!CHOH$—a liquid, boiling at 118.5° (245.3° F.), obtained by the hydrogenation of methyl-propylic acetone.

**Methyl-isopropyl Carbinol**— $(CH_3)_2{=}CH\overset{CH_3}{\diagup}CHOH$—obtained by the hydrogenation of methyl-isopropylic acetone; or by the action of hydriodic acid upon amylene, and the action of moist silver oxid upon the product so obtained. It is a colorless liquid, sp. gr. 0.829 at 0° (32° F.), having a pungent, ethereal odor; boils at 112.5° (234.5° F.), soluble in $H_2O$ and in alcohol.

**Ethyl-dimethyl Carbinol**—*Tertiary amylic alcohol*—*Amylene hydrate*—$CH_3-\overset{CH_3}{\underset{CH_3}{CH_2}}-COH$—is a liquid which solidifies at —12° (10.4° F.) and boils at 102.5° (216.5° F.); formed by the action of zinc methyl upon propionyl chlorid, or by decomposition of tertiary sulfamylic acid by boiling $H_2O$. The nitrite of this alcohol has been used as a substitute for amyl nitrite.

**Cetyl Hydroxid**—*Cetylic alcohol*—*Ethal*—$C_{16}H_{33}OH$—242—is obtained by the saponification of **spermaceti** (its palmitic ester). It is a white, crystalline solid; fusible at 49° (120.2° F.); insoluble in $H_2O$; soluble in alcohol and ether; tasteless and odorless.

**Ceryl Hydroxid**—$C_{27}H_{55}OH$—396—and **Miricyl Hydroxid**—$C_{30}H_{61}$—OH—438—are obtained as white crystalline solids; the former from China wax; the latter from beeswax, by saponification.

## DIATOMIC, OR DIHYDRIC ALCOHOLS; GLYCOLS.

The paraffin glycols are derived from the paraffins by the substitution of two hydroxyls for two H atoms. They bear the same relation to the monoatomic alcohols that the diacid bases bear to the monacid bases. They are diprimary, disecondary, primary-secondary, etc., according as they contain groups $CH_2OH$; CHOH, or COH. Their "Geneva" names are derived from those of the parent hydrocarbons by the substitution of the syllable "*diol*" for the terminal *e;* and they are distinguished as $\alpha$, $\beta$, $\gamma$, $\delta$, etc., according as the hydroxyls occupy 1:2,1:3,1:4,1:5, etc., positions. Thus the primary-secondary glycol $CH_2OH.CH_2.CHOH.CH_3$, is $\beta$-butandiol (p. 290).

They may be obtained from the neutral haloid esters by heating with silver acetate: $C_2H_4I_2+2AgC_2H_3O_2=2AgI+C_2H_4(C_2H_3O_2)_2$, and saponification of the ester so formed by caustic potash: $C_2H_4(C_2H_3O_2)_2+2KHO=C_2H_4(OH)_2+2KC_2H_3O_2$ (see p. 315).

While the monoatomic alcohols are only capable of forming a single ester with a monobasic acid, the glycols are capable of forming two such esters:

| | | |
|---|---|---|
| $CH_2(C_2H_3O_2)'$ | $CH_2(C_2H_3O_2)'$ | $CH_2(C_2H_3O_2)'$ |
| \| | \| | \| |
| $CH_3$ | $CH_2OH$ | $CH_2(C_2H_3O_2)'$ |
| Ethyl acetate. | Monoacetic glycol. | Diacetic glycol. |

**Methene Glycol**, which would have the composition $H_2C\langle^{OH}_{OH}$, is not known (p. 225). Its haloid esters are, however, known. A condensation product corresponding to it exists as **methene dimethylate**, $H_2C\langle^{OCH_3}_{OCH_3}$, also called **methylal** and **formal**, as a thin liquid, boiling at 42° (107.6° F.), soluble in alcohol, ether, and water, sp. gr. 0.855; formed by oxidizing methyl alcohol with $H_2SO_4$ and $MnO_2$. It has been used as a medicine.

**Ethene Glycol—Ethylene glycol, or alcohol, or hydroxid—** $\begin{matrix}CH_2OH\\|\\CH_2OH\end{matrix}$ **—62.**—This, the best known of the glycols, is prepared by the action of dry silver acetate upon ethylene bromid. The ester so obtained is purified by redistillation, and decomposed by heating for some time with barium hydroxid.

It is a colorless, slightly viscous liquid; odorless; faintly sweet; sp. gr. 1.125 at 0° (32° F.); boils at 197° (386.6° F.); sparingly soluble in ether; very soluble in water and in alcohol.

It is not oxidized by simple exposure to air, but on contact with platinum-black it is oxidized to glycolic acid; more energetic oxidants transform it into oxalic acid. Chlorin acts slowly upon glycol in the cold; more rapidly under the influence of heat, producing chlorinated and other derivatives. By the action of dry HCl upon cooled glycol, a product is formed, intermediate between it and ethylene chlorid, a neutral compound—**ethene chlorhydrin**, $\begin{matrix}CH_2OH\\|\\CH_2Cl\end{matrix}$, which boils at 130° (266° F.).

### TRIATOMIC, OR TRIHYDRIC ALCOHOLS; GLYCEROLS.

These are derived from the paraffins by the substitution of three hydroxyls for three hydrogen atoms, linked to different carbon atoms. The simplest triprimary glycerol, which would have the formula: $CH(CH_2OH)_3$, is unknown. The simplest known representative of the class is the ordinary glycerine, more properly called **glycerol**, which is diprimary-secondary. The relations of the monoatomic, diatomic, and triatomic alcohols to each other and to the parent hydrocarbon are shown in the following formulæ:

| | | | |
|---|---|---|---|
| $\begin{matrix}CH_3\\|\\CH_2\\|\\CH_3\end{matrix}$ | $\begin{matrix}CH_3\\|\\CH_2\\|\\CH_2OH\end{matrix}$ | $\begin{matrix}CH_2OH\\|\\CH_2\\|\\CH_2OH\end{matrix}$ | $\begin{matrix}CH_2OH\\|\\CHOH\\|\\CH_2OH\end{matrix}$ |
| Propane. | Propyl alcohol. | Propyl glycol. | Glycerol. |

The Geneva names of the glycerols are derived from those of the hydrocarbons by the substitution of the syllable "*triol*" for the terminal *e*. Thus glycerol is **propantriol.**

They are obtained by the saponification of their esters, either those existing in nature or those produced artificially.

They combine with acids to form three series of esters, known generically as **monoglycerids, diglycerids,** and **triglycerids,** formed by the combination of one molecule of the alcohol with one, two, or three molecules of a monobasic acid. The names of the individual esters terminate in *in*, and have a prefix indicating the number of acid residues. Thus: $C_3H_5(OH)_2.C_2H_3O_2$ is **monacetin,** $C_3H_5(OH)(C_2H_3O_2)_2$ is **diacetin,** and $C_3H_5(C_2H_3O_2)_3$ is **triacetin** (p. 316).

**Glycerol—Glycerin—Propenyl alcohol — Glycerinum** (U. S.)—$C_3H_5(OH)_3$—92—was first obtained as a secondary product in the manufacture of lead plaster; it is now produced as a by-product in the manufacture of soaps and of stearin candles. It exists free in palm-oil and in other vegetable oils. It is produced in small quantity during alcoholic fermentation, and is consequently present in wine and beer. It is much more widely disseminated in its esters, the neutral fats, in the animal and vegetable kingdoms.

It has been obtained by partial synthesis, by heating for some time a mixture of allyl tribromid, silver acetate and acetic acid, and saponifying the triacetin so obtained.

The glycerol obtained by the process now generally followed—the decomposition of the neutral fats and the distillation of the product in a current of superheated steam—is free from the impurities which contaminated the product of the older processes. The only impurities likely to be present are water, which may be recognized by the low sp. gr., and sometimes arsenic.

Glycerol is a colorless, odorless, syrupy liquid, has a sweetish taste; sp. gr. 1.26 at 15° (59° F.). Although it cannot usually be caused to crystallize by the application of the most intense cold, it does so sometimes under imperfectly understood conditions, forming small, white needles of sp. gr. 1.268, and fusible between 17° and 18° (62.6° and 64.6° F.). It is soluble in all proportions in water and alcohol, insoluble in ether and in chloroform. It is a good solvent for a number of mineral and organic substances (*glycerites* and *glyceroles*). It is not volatile at ordinary temperatures. When impure glycerol is heated, a portion distils unaltered at 275°–280° (527°–536° F.), but the greater part is decomposed into acrolein, acetic acid, carbon dioxid, and combustible gases. It may be distilled unchanged in a current of superheated steam between 285° and 315° (545°–599° F.). Pure glycerol distils unchanged at 290° at a pressure of 756 mm., and at 180° at 20 mm.

Concentrated glycerol, when heated to 150° (302° F.) ignites and burns without odor and without leaving a residue, and with a pale blue flame. It may also be burnt from a short wick.

Glycerol is readily oxidized, yielding different products with different degrees of oxidation. Platinum-black oxidizes it, with formation, finally, of $H_2O$ and $CO_2$. Oxidized by manganese dioxid and $H_2SO_4$, it yields $CO_2$ and formic acid. If a layer of glycerol diluted with an equal volume of $H_2O$ be floated on the surface of $HNO_3$ of sp. gr. 1.5, a mixture of several acids is formed: oxalic, $C_2O_4H_2$; glyceric, $C_3H_6O_4$; formic, $CH_2O_2$; glycollic, $C_2H_4O_3$; glyoxylic, $C_2H_4O_4$; and tartaric, $C_4H_6O_6$. When glycerol is heated with potassium hydroxid, a mixture of potassium acetate and formate is produced. When glycerol, diluted with 20 volumes of $H_2O$, is heated with Br; $CO_2$, bromoform, glyceric acid, and HBr are produced. Phosphoric anhydrid removes the elements of $H_2O$ from glycerol, with formation of acrolein (p. 372). A similar action is effected by heating with $H_2SO_4$, or with monopotassic sulfate. Heated with oxalic acid, glycerol yields $CO_2$ and formic acid.

The presence of glycerol in a liquid may be detected as follows: Add NaHO to feebly alkaline reaction, and dip into it a loop of Pt wire holding a borax bead; then heat the bead in the blow-pipe flame, which is colored green if the liquid contain $\frac{1}{100}$ of glycerol.

The glycerol used for medicinal purposes should respond to the following tests: (1) its sp. gr. should not vary much from that given above; (2) it should not rotate polarized light; (3) it should not turn brown when heated with sodium nitrate; (4) it should not be colored by $H_2S$; (5) when dissolved in its own weight of alcohol, containing one per cent. of $H_2SO_4$, the solution should be clear; (6) when mixed with an equal volume $H_2SO_4$, of sp. gr. 1.83, it should form a limpid, brownish mixture, but should not give off gas.

## POLYATOMIC, OR POLYHYDRIC ALCOHOLS.

**Tetratomic Alcohols** contain four hydroxyls. The best known is:

**Erythrol** — *Erythrite* — *Phycite* — *Erythroglucin* — $CH_2OH.(CHOH)_2.CH_2OH$ — which is a product of decomposition of erythrin, $C_{20}H_{22}O_{10}$, which exists in the lichens of the genus *rocella*. It crystallizes in large, brilliant prisms; very soluble in $H_2O$ and in hot alcohol, almost insoluble in ether; sweetish in taste; its solutions neither affect polarized light, nor reduce Fehling's solution, nor are capable of fermentation. Its watery solution, like that of sugar, is capable of dissolving a considerable quantity of lime, and from this solution alcohol precipitates a definite compound of erythrite and calcium. By oxidation with platinum-black it yields **erythroglucic acid**, $C_4H_8O_5$. With fuming $HNO_3$ it forms a tetranitro compound, which explodes under the hammer.

**Pentatomic, or Pentahydric Alcohols—Pentites**—contain five

hydroxyls. The only member of the group known to exist in nature is the simplest $C_5H_7(OH)_5$, called **adonite**, obtained from *Adonis vernalis*. Other members of the series are obtained by reduction of the corresponding aldopentoses (p. 264).

**Hexatomic, or Hexahydric Alcohols—Hexites**—contain six hydroxyls. They are closely related to the sugars (p. 265), which they resemble in their properties, although they do not reduce Fehling's solution, and are not fermented by yeast. They are obtained by reduction of the corresponding glucoses, aldohexoses and ketohexoses (p. 268). Three hexites occur in nature:

**Mannitol**—*Mannite*—$CH_2OH.(CHOH)_4.CH_2OH$—constitutes the greater part of manna, and also exists in a number of other plants. It is also produced during the so-called mucic fermentation of sugar, and during lactic fermentation. It crystallizes in long prisms, odorless, sweet; fuses at 166° (330.8° F.) and crystallizes on cooling; boils at 200° (396° F.), at which temperature it is converted into **mannitan**, $C_6H_{12}O_5$; soluble in $H_2O$, very sparingly in alcohol. When oxidized it yields first mannonic, then mannosaccharic acid (p. 297), and finally, oxalic acid. Organic acids combine with it to form esters.

**Sorbitol**—*Sorbite*—occurs in mountain-ash berries. It forms crystals, soluble in water.

**Dulcitol**—*Dulcite*—*Melampyrite*—*Dulcose*—*Dulcin*—exists in *melampyrum nemorosum*. It forms colorless, transparent prisms, fuses at 182° (359.6° F.), is odorless, faintly sweet, neutral in reaction, and optically inactive. It is subject to decompositions very similar to those to which mannite is subject, yielding **dulcitan**, $C_6H_{12}O_5$.

**Heptatomic, Octatomic and Nonatomic Alcohols**, containing respectively seven, eight and nine hydroxyls, are also known.

All polyatomic alcohols in solutions alkalized with caustic soda, when agitated with benzoyl chlorid, form insoluble benzoic esters, and, under proper conditions, the separation is quantitative, a fact which is utilized for their separation. The diamins (p. 330) behave similarly with benzoyl chlorid.

## ALDEHYDES AND KETONES.

The pure aldehydes and ketones, containing only CHO or CO and hydrocarbon groups, are to be considered rather as the second products of oxidation of the paraffins than as the first products of oxidation of the alcohols, primary or secondary. While the distinction is not material with the aldehydes derivable from the monoatomic alcohols, it is so with similar derivatives of alcohols of higher atom-

icity and with the ketones, which may be either pure aldehydes or ketones, or, if they retain alcoholic groups, substances of mixed function: aldehyde-alcohols and ketone-alcohols. Thus from the hydrocarbons the following may be derived:

$2(CH_3.CH_3)+O_2=2(CH_3.CH_2OH)$ = Alcohols—$C_nH_{2n+2}O$,
$CH_3.CH_3+O_2=H_2O+CH_3.CHO$ = Aldehydes—$C_nH_{2n}O$,
$CH_3.CH_3+2O_2=2H_2O+CHO.CHO$ = Glyoxals—$C_nH_{2n-2}O_2$,
$CH_3.CH_2.CH_3+O_2=H_2O+CH_3.CO.CH_3$ = Ketones—$C_nH_{2n}O$,

and from the alcohols not only the above, but also substances such as

$2(CH_2OH.CH_2OH)+O_2=2H_2O+2(CHO.CH_2OH)$=Glycolyl aldehyde,
$2(CH_2OH.CHOH.CH_2OH)+O_2=2H_2O+2(CHO.CHOH.CH_2OH)$=Glycerol aldehyde,
$2(CH_2OH.CHOH.CH_2OH)+O_2=2H_2O+2(CH_2OH.CO.CH_2OH)$ =Glycerol ketone.

The aldehydes and ketones are isomeric with each other and also with the allyl alcohols, $CH_2:CH.CH_2OH$, and the methylene oxids, $(CH_2)_x:O$.

Both aldehydes and ketones contain the carbonyl group CO, which in the ketone is united to two alkyls, $CH_3.CO.CH_3$; and in the aldehyde to one alkyl and a hydrogen atom, $CH_3.CO.H$.

The aldehydes and ketones react with hydroxylamin to form aldoxisms and ketoxims (p. 360), and with phenylhydrazin to form phenylhydrazones (p. 429). Both of these reactions are extensively used for the identification of these bodies.

### ALDEHYDES.

The name "aldehyde" is a contraction of "alcohol dehydrogenatum," derived from the method of formation of these bodies by removal of hydrogen from alcohol.

The aldehydes are formed: (1) By the limited oxidation of the corresponding alcohols: $2CH_3.CH_2OH+O_2=2CH_3.CHO+2H_2O$; (2) By the action of nascent hydrogen upon the corresponding acidyl chlorids (p. 311), or anhydrids (p. 310): $CH_3.CO.Cl+H_2=CH_3.CHO+HCl$, or $(CH_3.CO)_2O+2H_2=2CH_3.CHO+H_2O$; (3) By the distillation of a mixture of calcium formate and the Ca salt of the corresponding acid: $(H.COO)_2Ca+(CH_3.COO)_2Ca=2CO_3Ca+2CH_3.CHO$.

The aldehydes, being intermediate between the alcohols and acids, are readily converted into the former by the action of reducing agents: $CH_3.CHO+H_2=CH_3.CH_2OH$; or into the latter by oxidation: $2CH_3.CHO+O_2=2CH_3.COOH$. The facility with which the aldehydes are oxidized renders them active reducing agents.

They combine with the monometallic alkaline sulfites to form crystalline compounds, whose formation is frequently resorted to for their separation and purification: $CH_3.CHO+SO_3HNa=CH_3.CH\begin{matrix}OH\\SO_3Na\end{matrix}$.

They unite directly with ammonia to produce crystalline compounds called **aldehyde ammonias** (p. 360): $CH_3.CHO + NH_3 = CH_3.CH\langle^{OH}_{NH_2}$.

Chlorin and bromin displace the hydrogen of the aldehydic group with formation of acidyl chlorids or bromids: $CH_3.CHO + Cl_2 = CH_3.CO.Cl + HCl$. The oxygen of the same group may also be displaced by chlorin, by the action of phosphorus pentachlorid, with formation of paraffin dichlorids: $CH_3.CHO + PCl_5 = CH_3.CHCl_2 + POCl_3$. By indirect means compounds may also be obtained in which the hydrogen of the hydrocarbon group is substituted by chlorin, as chloral is obtained from ethylic alcohol: $CH_3.CH_2OH + 4Cl_2 = CCl_3.CHO + 5HCl$.

The aldehydes polymerize readily, forming cyclic compounds, as trioxymethylene is formed by formic aldehyde: $3H.CHO = O\langle^{CH_2.O}_{CH_2.O}\rangle CH_2$. Or two aldehyde molecules may condense, by union through carbon atoms, to form **oxyaldehydes** (p. 263), as aldol is formed by condensation of acetic aldehyde: $2CH_3.CHO = CH_3.CHOH.CH_2.CHO$.

Hydrocyanic acid combines with the aldehydes (and ketones) to produce **oxycyanids**, or nitrils of the oxyacids: $CH_3.CHO + HCN = CH_3.CH\langle^{OH}_{CN}$, which, in turn, are decomposable by acids or alkalies with formation of the α-oxyacids (p. 291).

**Formaldehyde**—*Formyl hydrid*—H.CHO—30—is formed when air charged with vapor of methylic alcohol is passed over an incandescent platinum wire. It is also produced by the dry distillation of calcium formate: $(H.COO)_2Ca = CaCO_3 + H.COH$. By strong cooling, it condenses to a colorless liquid, which boils at—21° (—5.8° F.). It has a sharp, penetrating odor, and is an active germicide. It is extensively used as an antiseptic and disinfectant, either in the gaseous form or in aqueous solution. The commercial **formaline** is a 40% solution.

Formaldehyde polymerizes with great readiness by moderate elevation of temperature to form **paraformaldehyde**, or **trioxymethylene**, $O\langle^{CH_2.O}_{CH_2.O}\rangle CH_2$, which is also obtained as a crystalline substance, fusing at 152° (305.6° F.), insoluble in $H_2O$, alcohol and ether, by distilling glycollic acid with $H_2SO_4$, or by the action of silver oxalate or oxid on methene iodid: $CH_2I_2 + Ag_2O = H.CHO + 2AgI$.

**Acetaldehyde—Acetic Aldehyde**—*Acetyl hydrid*—$CH_3.CHO$—44—is formed in all reactions in which alcohol is deprived of H without introduction of O. It is prepared by distilling from a capacious retort, connected with a well-cooled condenser, a mixture of $H_2SO_4$, 6 pts.; $H_2O$, 4 pts.; alcohol, 4 pts., and powdered manganese dioxid, 6 pts. The product is redistilled from calcium chlorid below 50° (122° F.).

The second distillate is mixed with two volumes of ether, cooled by a freezing mixture, and saturated with dry $NH_3$; there separate crystals of **aldehyde ammonia**, $CH_3.CH\langle^{NH_2}_{OH}$, which are washed with ether, dried and decomposed in a distilling apparatus, over the water-bath, with the proper quantity of dilute $H_2SO_4$; the distillate is finally dried over calcium chlorid and rectified below 35° (95° F.).

Aldehyde is a colorless, mobile liquid; has a strong, suffocating odor; sp. gr. 0.790 at 18° (64.4° F.); boils at 21° (69.8° F.); soluble in all proportions in water, alcohol and ether. If perfectly pure, it may be kept unchanged; but if an excess of acid have been used in its preparation, it gradually decomposes. When heated to 100° (212° F.), it is decomposed into water and crotonic aldehyde.

In the presence of nascent H, aldehyde takes up $H_2$, and regenerates alcohol. Cl converts it into acetyl chlorid, $C_2H_3O.Cl$, and other products. Oxidizing agents convert it into acetic acid. At the ordinary temperature $H_2SO_4$; HCl; and $SO_2$ convert it into a colorless liquid called **paraldehyde** $(C_2H_4O)_3$, which boils at 124° (255.2° F.), and is more soluble in cold than in warm water. The same reagents, acting upon aldehyde at temperatures below 0° (32° F.) convert it into **metaldehyde** $(C_2H_4O)_n$. When heated with potassium hydroxid, aldehyde becomes brown, a brown resin separates, and the solution contains potassium formate and acetate. If a watery solution of aldehyde be treated, first with $NH_3$ and then with $H_2S$, a solid, crystalline base, **thialdin**, $C_6H_{13}NS_2$, separates. It also forms crystalline compounds with the alkaline bisulfites. It decomposes solutions of silver nitrate, separating the silver in the metallic form, and under conditions which cause it to adhere strongly to glass.

Vapor of aldehyde, when inhaled in a concentrated form, produces asphyxia, even in comparatively small quantity. When diluted with air it is said to act as an anæsthetic. When taken internally it causes sudden and deep intoxication, and it is to its presence that the first products of the distillation of spirits of inferior quality owe in a great measure their rapid, deleterious action.

**Trichloraldehyde**—*Trichloracetyl hydrid*—**Chloral**—$CCl_3.CHO$—147.5—is one of the final products of the action of Cl upon alcohol, and is obtained by passing dry Cl through absolute alcohol to saturation; applying heat toward the end of the reaction, which requires several hours for its completion. The liquid separates into two layers; the lower is removed and shaken with an equal volume of concentrated $H_2SO_4$ and again allowed to separate into two layers; the upper is decanted; again mixed with $H_2SO_4$, from which it is distilled; the distillate is treated with quicklime, from which it is again distilled, that portion which passes over between 94° and 99°

(201.2°–210.2° F.) being collected. It sometimes happens that chloral in contact with $H_2SO_4$ is converted into a modification, insoluble in $H_2O$, known as **metachloral**; when this occurs it is washed with $H_2O$, dried and heated to 180° (356° F.), when it is converted into the soluble variety, which distils over.

Chloral is a colorless liquid, unctuous to the touch; has a penetrating odor and an acrid, caustic taste; sp. gr. 1.502 at 18° (64.4° F.); boils at 97° (206.6° F.), very soluble in water, alcohol, and ether; dissolves Cl, Br, I, S, and P. Its vapor is highly irritating. It distils without alteration.

Although chloral has not been obtained by the direct substitution of Cl for H in aldehyde, its reactions show it to be an aldehyde. It forms crystalline compounds with the bisulfites; it reduces solutions of silver nitrate in the presence of $NH_3$; $NH_3$ and $H_2S$ form with it a compound similar to thialdin; with nascent H it regenerates aldehyde; oxidizing agents convert it into trichloracetic acid. Alkaline solutions decompose it with formation of chloroform and a formate.

With a small quantity of $H_2O$ chloral forms a solid, crystalline hydrate, heat being at the same time liberated. This hydrate has the composition $C_2HCl_3O.H_2O$, and its constitution, as well as that of chloral itself, is indicated by the formulæ:

| $CH_3$ | $CCl_3$ | $CCl_3$ |
|---|---|---|
| \| | \| | \| |
| $CHO$ | $CHO$ | $CH(OH)_2$ |
| Aldehyde. | Trichloraldehyde (chloral). | Chloral hydrate. (See p. 225). |

**Chloral Hydrate—Chloral** (U. S.)—is a white, crystalline solid; fuses at 57° (134.6° F.); boils at 98° (208.4° F.), at which temperature it suffers partial decomposition into chloral and $H_2O$; volatilizes slowly at ordinary temperatures; is very soluble in $H_2O$; neutral in reaction; has an ethereal odor, and a sharp, pungent taste. Concentrated $H_2SO_4$ decomposes it with formation of chloral and **chloralid.** $HNO_3$ converts it into trichloracetic acid. When pure it gives no precipitate with silver nitrate solution, and is not browned by contact with concentrated $H_2SO_4$. Under the influence of sunlight it is violently decomposed by potassium chlorate; chlorin, phosgene gas, carbon dioxid, and chloroform are given off, and after a time, crystals of potassium trichloracetate separate from the cooled mixture.

Chloral also combines with alcohol, with elevation of temperature, to form a solid, crystalline body—**chloral alcoholate**: $CCl_3CH\langle^{OH}_{O-C_2H_5}$.

**Action of Chloral Hydrate upon the Economy.**—Although it was the ready decomposition of chloral into a formate and chloroform which first suggested its use as a hypnotic to Liebreich, and although

this decomposition was at one time believed to occur in the body under the influence of the alkaline reaction of the blood, more recent investigations have shown that the formation of chloroform from chloral in the blood is, to say the least, highly improbable, and that chloral has, in common with many other chlorinated derivatives of this series, the property of acting directly upon the nerve-centers.

Neither the urine nor the expired air contains chloroform when chloral is taken internally; and when taken in large doses, chloral appears in the urine. The fact that the action of chloral is prolonged for a longer period than that of the other chlorinated derivatives of the fatty series is probably due, in a great measure, to its less volatility and less rapid elimination.

When taken in overdose, chloral acts as a poison, and its use as such is rapidly increasing as acquaintance with its powers becomes more widely disseminated. A strong aqueous solution is frequently added by criminals to intoxicants to deprive their victims of consciousness (knock-out drops).

No chemical antidote is known. The treatment should be directed to the removal of any chloral remaining in the stomach by the syphon, and to the maintenance or restoration of respiration.

In fatal cases of poisoning by chloral that substance may be detected in the blood, urine, and contents of the stomach by the following method: the liquid is rendered strongly alkaline with potassium hydroxid: placed in a flask, which is warmed to 50°–60° (122°–140° F.), and through which a slow current of air, heated to the same temperature, is made to pass; the air, after bubbling through the liquid, is tested for chloroform by the methods described on page 235. As chloral distils with vapor of water from acid solutions, and as it gives the same reactions as chloroform, except the fluorescence with the resorcinol reaction (p. 235), the presence of chloral as such can only be positively demonstrated by extraction of the crystals of the hydrate by ether, and spontaneous evaporation of the ethereal solution.

**Bromal**—$CBr_3.CHO$—281.—A colorless, oily, pungent liquid: sp. gr. 3.34; boils at 172° (341.6° F.); neutral; soluble in $H_2O$, alcohol, and ether. It combines with $H_2O$ to form **bromal hydrate**, $CBr_3.CH(OH)_2$; large transparent crystals; soluble in $H_2O$; decomposed by alkalies into bromoform and a formate. Produces anæsthesia without sleep; very poisonous.

**Thioaldehydes.**—By the action of $H_2S$ on aldehyde in the presence of HCl two products are obtained, having the composition $(CH_3CHS)_3$, known as $\alpha$ and $\beta$ **Trithioacetaldehyde.** The former is in large prismatic crystals, fusible at 101° (213.8° F.), the latter in long needles, fusible at 125°–126° (257°–258.8° F.).

**Propaldehyde—Propionic aldehyde**—$CH_3.CH_2.CHO$—58—obtained by the general reaction from propylic alcohol, is a colorless liquid, resembling acetic aldehyde; boils at 40° (120.2° F.).

**Normal Butaldehyde—Butyric aldehyde**—$CH_3.CH_2.CH_2.CHO$—72—is an oily liquid, boiling at 73° (163.4° F.). Its trichlorinated derivative, **Trichlorbutaldehyde**, or **Butyric chloral**, $CCl_3.CH_2.CHO$—is the substance whose hydrate is used as a medicine under the name **croton chloral hydrate.** It is a colorless liquid, boiling at 160° (320° F.), obtained by the action of Cl on acetaldehyde.

**Acetals.**—The chloral alcoholate referred to above (p. 259) is a mono-ether of chloral hydrate $CCl_3.CH\langle^{OH}_{OC_2H_5}$, whose corresponding di-ether is $CCl_3.CH\langle^{OC_2H_5}_{OC_2H_5}$, **trichloracetal.** The *acetals* are substances derived from the hypothetical aldehyde hydrates, corresponding to chloral hydrates, by the substitution of alkyls for the hydrogens of the hydroxyls.

**Methylal—Formal**—$CH_2\langle^{OCH_3}_{OCH_3}$—76—is formed by distilling a mixture of $MnO_2$, methyl alcohol, $H_2SO_4$ and $H_2O$. It is a colorless liquid; sp. gr. 0.8551 at 17° (62.6° F.); boiling at 42° (107.6° F.); soluble in $H_2O$, alcohol, and oils. It has a burning, aromatic taste, and an odor resembling those of chloroform and acetic acid. It has been used as a hypnotic.

**Acetal**—$CH_3.CH\langle^{OC_2H_5}_{OC_2H_5}$—104—a colorless liquid, boils at 104° (219.2° F.), sp. gr. 0.8314; sparingly soluble in $H_2O$, readily in alcohol; obtained by heating a mixture of aldehyde, alcohol and glacial acetic acid, or in the same manner as formal, using ethylic in place of methylic alcohol.

**Dialdehydes**—containing two CHO groups, such as **Glyoxal**—CHO.CHO, are also known.

## KETONES OR ACETONES.

These substances all contain the group of atoms $(CO)''$ uniting two hydrocarbon groups, and their constitution may be represented graphically thus:

| | | |
|---|---|---|
| OH | $CH_3$ | $CH_3$ |
| \| | \| | \| |
| CO | CO | CO |
| \| | \| | \| |
| $CH_3$ | $CH_3$ | $CH_2$ |
| | | \| |
| | | $CH_3$ |
| Acetic Acid. | Dimethyl ketone (acetone). | Methyl-ethyl ketone. |

the first being a **symmetrical ketone** and the latter an **unsymmetrical.** The ketones are isomeric with the aldehydes, from which they are distinguished: (1) by the action of nascent H, which pro-

duces a primary alcohol with an aldehyde, and a secondary alcohol with a ketone; (2) by the action of O, which unites directly with an aldehyde to produce the corresponding acid, while it causes the disruption of the molecule of the ketone, with formation of two acids.

**Dimethyl Ketone—Acetone**—*Acetylmethylid—Pyroacetic ether* or *spirit*—$CO\langle^{CH_3}_{CH_3}$—58—is formed as one of the products of the dry distillation of the acetates; by the decomposition of the vapor of acetic acid at a red heat; by the dry distillation of sugar, tartaric acid, etc.; and in a number of other reactions. It is obtained by distilling dry calcium acetate. It is also formed in large quantity in the preparation of anilin.

It is a limpid, colorless liquid; sp. gr. 0.7921 at 18° (64.4° F.); boils at 56° (132.8° F.); soluble in $H_2O$, alcohol and ether; has a peculiar ethereal odor and a burning taste; is a good solvent of resins, fats, camphor, gun-cotton; readily inflammable. It forms crystalline compounds with the alkaline bisulfites. Cl and Br, in the presence of alkalies, convert it into chloroform or bromoform; Cl alone produces with acetone a number of chlorinated products of substitution. Certain oxidizing agents transform it into a mixture of formic and acetic acids; others into oxalic acid.

Acetone has been found to exist in the blood and urine in certain pathological conditions, and notably in diabetes. The peculiar odor exhaled by diabetics is produced by this substance, which has also been considered as being the cause of the respiratory derangements and coma which frequently occur in the last stages of the disease.

That acetone exists in the blood in such cases is certain: it is not certain, however, that its presence produces the condition designated as **acetonæmia**. It can hardly be doubted that the acetone thus existing in the blood is indirectly formed from diabetic sugar, and it is probable also that a complex acid, known as **ethyldiacetic**, $C_6H_9O_3H$, is formed as an intermediate product.

See aromatic ketones.

**Diketones**, containing two CO groups, such as $CH_3.CO.CO.CH_3$, **triketones**, such as $CH_3.CO.CO.CO.CH_3$, and **tetraketones**, such as $CH_3.(CO)_4.CH_3$, are also known.

### ALDEHYDE-ALCOHOLS, KETONE-ALCOHOLS, ALDEHYDE-KETONES, AND OXYALDEHYDE-KETONES.

These bodies are, as the names indicate, substances of mixed function. The known oxyaldehyde-ketones, aldehyde-ketones, and such of the aldehyde- and ketone-alcohols as contain hydrocarbon groups are neither numerous nor important. The following formulæ indicate their structure:

| | | | |
|---|---|---|---|
| CHO<br>\|<br>CO<br>\|<br>$CH_2OH$ | CHO<br>\|<br>CO<br>\|<br>$CH_3$ | CHO<br>\|<br>CHOH<br>\|<br>$C_2H_5$ | $CH_2OH$<br>\|<br>CO<br>\|<br>$CH_3$ |
| Oxyaldehyde-ketone. | Aldehyde-ketone. | Aldehyde-alcohol. | Ketone alcohol. |
| Oxypyroracemic aldehyde. | Methyl Glyoxal. | Aldol. | Acetol. |

The aldehyde-alcohols, such as aldol and glycolyl aldehyde: $CH_2OH.CHO$, are called **oxyaldehydes.**

On the other hand, some of the more important of the carbohydrates, such as glucose, maltose and fructose, are hexatomic aldehyde-alcohols, or ketone-alcohols, in which all of the groups are oxidized.

## CARBOHYDRATES.

The definition of the term **carbohydrate** as "a substance of unknown constitution composed of carbon, hydrogen and oxygen, in which the oxygen and hydrogen are in the same proportion as in water" was self-destructive so soon as the constitution of these substances should become known, as it now has. Yet the first words of the definition were necessary to exclude substances such as acetic acid, $C_2H_4O_2$, which would otherwise accord with the definition, yet were never considered as carbohydrates. But, while the sugars and starches have been thus removed from the "miscellaneous" residuum of our chemical classification, they are still conveniently referred to as carbohydrates in physiological chemistry.

The carbohydrates are classified into:

**Monosaccharids,** or **Monoses**—which do not yield any other sugar or sugars by the action upon them of dilute acids (glucose, fructose, galactose, etc.);

**Disaccharids,** or **Saccharobioses**—which, under the influence of dilute acids, take up $H_2O$ and yield two other sugar molecules (saccharose, lactose, maltose, etc.);

**Trisaccharids,** or **Saccharotrioses**—which, under the same influence, take up $2H_2O$ and yield three other sugar molecules; and

**Polysaccharids**—which, under the same influence, take up more than $2H_2O$, and yield more than three sugar molecules (starches, gums, celluloses, etc.).

The disaccharids, trisaccharids and polysaccharids may be considered as produced by the fusion of two or more monosaccharid molecules with elimination of one or more molecules of water.

Those carbohydrates which contain the ketone group, CO, are called **ketoses,** those containing the aldehyde group, CHO, **aldoses.** The names of all carbohydrates terminate in **ose.**

## MONOSACCHARIDS—MONOSES

**Monosaccharids are bioses, trioses, tetroses, pentoses, hexoses, heptoses, octoses or nonoses according as they contain from two to nine carbon atoms:**

*Aldoses.*

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| CHO | CHO | CHO | CHO | CHO | CHO | CHO | CHO |
| $CH_2OH$ | CHOH | $(CHOH)_2$ | $(CHOH)_3$ | $(CHOH)_4$ | $(CHOH)_5$ | $(CHOH)_6$ | $(CHOH)_7$ |
| | $CH_2OH$ | $CH_2OH$ | $CH_2OH$ | $CH_2OH$ | $CH_2OH$ | $CH_2OH$ | $CH_2OH$ |

*Ketoses.*

| | | | | | | |
|---|---|---|---|---|---|---|
| $CH_2OH$ | $CH_2OH$ | $CH_2OH$ | $CH_2OH$ | $CH_2OH$ | $CH_2OH$ | $CH_2OH$ |
| CO | CO | CO | CO | CO | CO | CO |
| $CH_2OH$ | CHOH | $(CHOH)_2$ | $(CHOH)_3$ | $(CHOH)_4$ | $(CHOH)_5$ | $(CHOH)_6$ |
| | $CH_2OH$ | $CH_2OH$ | $CH_2OH$ | $CH_2OH$ | $CH_2OH$ | $CH_2OH$ |
| Bioses. | Trioses. | Tetroses. | Pentoses. | Hexoses. | Heptoses. | Octoses. | Nonoses. |

The monosaccharids are neutral substances, sweet, odorless, white, insoluble in ether, sparingly soluble in alcohol, and readily soluble in water. Like all aldehydes and ketones, they are readily oxidized, and in their oxidation act as reducing agents. It is upon this quality that the several "reduction tests," such as Trommer's, Fehling's, Barfoed's, Boettger's, Mulder-Neubauer's, etc., are based. Another quality of the monosaccharids, utilized for their separation and identification, is that they all give crystalline precipitates of substances called **osazones** when their solutions, acidulated with acetic acid, are heated with phenyl-hydrazin, $C_6H_5.H:N.N:H_2$. The trioses, hexoses and nonoses are capable of alcoholic fermentation, the others are not. Most of the monosaccharids are optically active.

### DIOSES, TRIOSES, TETROSES AND PENTOSES.

**Glycolyl aldehyde**, $CH_2OH.CHO$, is the only **diose** possible. It is produced by the action of baryta water upon brom-acetaldehyde.

The two possible **trioses: Glycerol aldehyde**, $CHO.CHOH.CH_2OH$, and **Glycerol ketone**, $CH_2OH.CO.CH_2OH$, are not known in the pure state, but a mixture of the two is produced when glycerol is oxidized by dilute nitric acid.

Similarly **erythrose** is a mixture of the two **tetroses**, $CHO.(CHOH)_2.CH_2OH$ and $CH_2OH,CHOH.CO.CH_2OH$, formed by oxidation of erythrol by dilute nitric acid.

The **pentoses** hitherto described are all aldo-pentoses, $C_4H_5(OH)_4.CHO$, although keto-pentoses probably also exist. When

distilled with hydrochloric or dilute sulfuric acid they yield furfurole: $CHO.(CHOH)_3.CH_2OH = 3H_2O + CHO.C\begin{matrix} CH{:}CH \\ \diagup \quad | \\ \diagdown \quad | \\ CH.O \end{matrix}$ ; a reaction which is utilized for their quantitative determination. **Arabinose** is a pentose obtained by the action of dilute sulfuric acid upon cherry gum. **Xylose,** or wood sugar, is produced by boiling wood-gum with dilute acid. **Ribose** is a synthetic product. **Rhamnose,** or **Isodulcite, Chinovose,** and **Fucose** are methyl-pentoses: $CH_3.(CHOH)_4.CHO$, obtained by the decomposition of certain glucosids or from sea weeds. These pentoses result from the hydrolysis of pentosanes, polysaccharids occurring as gums in plants. Pentoses have also been found in the urine, particularly in diabetes and after the use of certain fruits containing pentosanes. They are also among the products of decomposition of certain nucleoproteids. Pentoses, when warmed with hydrochloric acid in presence of phloroglucin, give a fine red color, and a sharp absorption band near the Na line.

### HEXOSES—GLUCOSES.

In this class are included some well-known sugars, such as glucose and fructose, which occur free in the vegetable world. They exist in ether-like combination in many of the **glucosids** (p. 409).

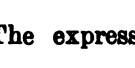
They are mostly sweet, crystalline substances, very soluble in water, and difficultly soluble in alcohol. They are formed by (1) the hydrolysis of the di- and polysaccharids: $C_{12}H_{22}O_{11} + H_2O = 2C_6H_{12}O_6$, or $n(C_6H_{10}O_5) + nH_2O = {}_2nC_6H_{12}O_6$; (2) by oxidation of the corresponding hexatomic alcohol; (3) by reduction of the lactones of the monocarboxylic acids (p. 320).

They exhibit the usual reactions of the alcohols and those of the aldehydes or ketones. On reduction they produce hexatomic alcohols; and on oxidation they yield monocarboxylic acids. Their alcoholic hydrogen is replaceable by certain metals with formation of **saccharates,** corresponding to the alcoholates (p. 244). With acids they yield esters. They form **osazones** with phenylhydrazin. Some are very prone to alcoholic fermentation: $C_6H_{12}O_6 = 2C_2H_6O + 2CO_2$, while others readily undergo lactic fermentation: $C_6H_{12}O_6 = 2C_3H_6O_3$. Being polyatomic alcohols, the hexoses form insoluble benzoic esters when their alkaline solutions are shaken with benzoyl chlorid (p. 255).

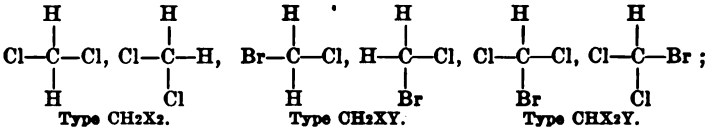
Of the described hexoses, mannose, glucose, gulose, idose, galactose and talose are aldoses; fructose and sorbinose are ketoses.

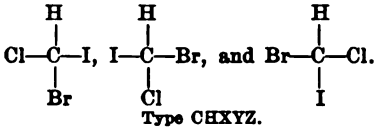
**Optical Activity.**—All of the hexoses exist in three isomerids, differing from each other in their action upon polarized light. One of these rotates the plane of polarization to the right, and is designated as the dextro-, or d-compound; another is lævogyrous and is

designated as the lævo-, or l-compound, while the third is inactive, and is distinguished by the symbol (d+l).

**Stereoisomerism, or Space Isomerism.**—The graphic formulæ indicate the structure of the molecule only partially; they show that certain atoms in the molecule are attached to some of their fellows more closely than to others, but they give no indication of the positions which the atoms occupy in space with regard to each other. The expression  , the most completely detailed graphic representation of that group, indicates at the most that the two hydrogen atoms are attached to one side of the carbon atom, while the hydroxyl is attached to another. **Stereochemistry** is that branch of chemistry treating of the relations of the atoms to each other *in space*. It has been greatly developed in recent years and affords, among other things, the first rational explanation of the cause of the differences in the optical activity of the hexoses, as well as of lactic and tartaric acids, and of many other substances.

If we suppose that differences in the relative positions which atoms or groups attached to carbon atoms occupy with relation to each other produce different compounds (see Place Isomerism, p. 290; Orientation, p. 381); and if we also suppose that the four valences of the carbon atom act in a plane, and at right angles to each other, a vast number of space-isomerids of the di- and poly-substituted derivatives of the aliphatic hydrocarbons would exist, no representatives of which are, however, known. For example, marsh-gas would yield two isomerids of each of the types: $CH_2X_2$, $CH_2XY$ and $CH(X)_2Y$, and three isomerids of the type CHXYZ, in which X, Y, and Z represent any three univalent atoms or radicals, thus:




But only one representative of each of these types is known. Therefore the usual graphic representation of the valences of the carbon atom as above, while convenient, is not *spatially* consistent with fact, and the four valences of the carbon atom are not exerted in one plane.

The suggestion of Van't Hoff (following the somewhat similar

idea of Kekulé) that the valences of the carbon atom are represented by considering it as occupying the interior of a regular tetrahedron, the solid angles of which indicate the direction of its valences (Fig. 34, A), taken in connection with the hypothesis of an **asymmetric carbon atom**, affords a rational explanation of the facts just cited, and of the differences in the optical properties of the substances mentioned.

Admitting the regular tetrahedron to represent the arrangement of the valences of the carbon atom, it follows that all carbon atoms, two of whose valences are satisfied by the same kind of univalent atom or group, and the other two by two constant but dissimilar univalents, must be symmetrical. The two similar univalents must occupy the summits at the extremities of some one crest, and the only possible variation in arrangement of the other two is in their position with regard to this crest. Thus B and C, Fig. 34, although dissimilar in the position in which they are placed, become perfectly symmetrical when either one is rotated through 180 degrees. But when all four of the carbon valences are satisfied by different univalents two arrangements are possible, producing two molecular groups which are unsymmetrical in whatever position they may be placed. Thus D and E, Fig. 34, are unsymmetrical in the positions in which they are represented, and remain so, however their positions may be changed. A **carbon** atom attached to four different univalents is called an **asymmetric carbon atom.** In graphic formulæ asymmetric carbon atoms are designated by the italic *C*, or by an asterisk, C*. Substances containing an asymmetric carbon atom exist in two oppositely optically active modifications.

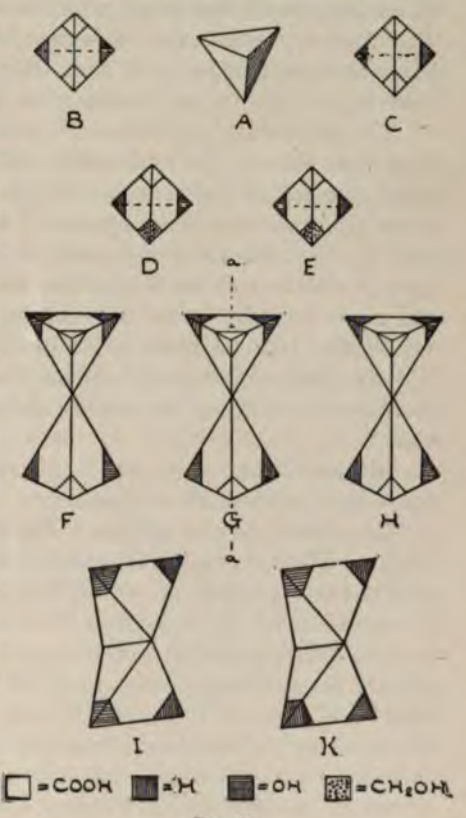



FIG. 34.

The structure of the four isomeric tartaric acids (p. 295) was first

explained under the hypothesis of the asymmetric carbon atom. Let it be assumed that two asymmetric carbon atoms, with their attached groups or atoms, exert a "directing influence" upon each other, and that, being attached to each other at one point only, they are capable of rotating independently about a common axis (*a.a.* Fig. 34, G), such rotation would then occur in obedience to the directing influence until a condition of equilibrium is reached, in which position the atoms would remain. Assuming this position to be that shown in F, G, and H, Fig. 34, with the two COOH groups in like relation, then the three unsymmetrical arrangements shown in the figure are possible. The first represents the structure of dextro-tartaric acid, G that of lævo-tartaric acid, and H that of meso-tartaric acid, while racemic acid is a combination of dextro- and lævo-tartaric acids.

The tetrahedron representation of the carbon valences adapts itself very well also to the explanation of certain isomerids of the ethylene series, in which two carbon atoms are doubly linked together. In these the two carbon atoms being linked together at two points (I and K, Fig. 34) cannot be considered as being capable of rotation, and, if the two other valences of each carbon atom are satisfied by the same two dissimilar univalents, two positions are possible: I, in which the like univalents are directed to the same side, called the "plane symmetrical configuration," and K, in which they are directed towards opposite sides, called the "axially symmetrical configuration."

**Mannose** is obtained, as d-, l-, and d+l, mannoses by oxidation of the corresponding mannitols.

**Glucose — Grape Sugar — Dextrose — Liver Sugar — Diabetic Sugar**—d-Glucose occurs in many sweet fruits and vegetable juices, and in honey, accompanied by fructose; and, in the animal world, in the contents of the intestine, liver, bile, thymus, heart, lungs, blood, and, in small quantity, in the urine. Pathologically, it appears in the saliva, perspiration, fæces, and, in largely increased amount, in the blood and urine in diabetes mellitus. It is produced by the decomposition of the polysaccharids and of many of the glucosids, and is manufactured on a large scale by the action of boiling dilute $H_2SO_4$ upon starch. The commercial product so obtained is either an amorphous, white solid (grape sugar), containing about 60% of true glucose, along with dextrins and the unfermentable **isomaltose**, or **gallisin**, $C_{12}H_{22}O_{11}$; or a thick, colorless syrup (glucose), containing, besides the above, a minute quantity of a nitrogenous body which exerts a solvent action upon coagulated albumin at the body temperature.

*d-Glucose* has been produced synthetically by the reduction of the lactone of d-gluconic acid (p. 294).

It crystallizes from its aqueous solutions at the ordinary temperature with difficulty in white, opaque, spheroidal masses containing 1Aq, which fuse at 86° and lose the Aq at 110°. From its concentrated aqueous solution at 30° to 35°, or from its alcoholic solution it crystallizes in hard, anhydrous, crystalline crusts, which fuse at 146°. It is soluble in all proportions in hot water, is very soluble in cold water, and soluble in alcohol. It is less sweet and less soluble than cane sugar. Its aqueous solutions are dextrogyrous: $[a]_D=+52.6°$ in boiled solutions. Freshly prepared cold aqueous solutions have nearly double that rotary power at first, the value of $[a]_D$ gradually falling to 52.6° in about twenty-four hours. Its osazone, d-glucosazone, crystallizes in needles, fusible at 205°. Its solutions dissolve baryta and lime, with which, as with potash, soda, and the oxids of Pb and Cu, it forms **saccharates.**

*l-Glucose* is formed by reduction of the lactone of l-gluconic acid. It is in all respects similar to d-glucose except that it fuses at 143°, and its solutions are lævogyrous $[a]_D=-51.4°$.

*d+l-Glucose* is formed by reduction of d+l-gluconic lactone; or by union of d- and l-glucose. Its solutions are optically inactive.

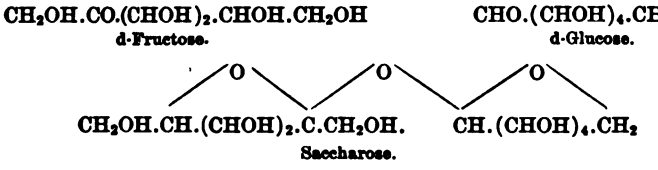
**Galactose** is also known in its three modifications. d-Galactose is produced by the hydrolysis of milk sugar and of certain gums. It crystallizes more readily than glucose, is very sparingly soluble in cold alcohol, has a specific rotary power of $[a]_D=+83.33°$, and fuses at 160°. By reduction it yields dulcite, and by oxidation galactonic acid, $CH_2OH.(CHOH)_4.COOH$, and mucic acid, $COOH.(CHOH)_4.COOH$. **Cerebrose,** obtained by the hydrolysis of **cerebrin,** a constituent of nerve tissue, is identical with galactose.

**Fructose,** a ketohexose, exists in the three modifications. *d-Fructose—Lævulose—Fruit sugar*—forms the uncrystallizable portion of the sugar of fruits and of honey, in which it is associated with glucose; it is produced artificially by the prolonged action of boiling water upon **inulin,** a polysaccharid; also, along with an equal quantity of glucose, as one of the constituents of **invert sugar,** by the decomposition of cane sugar; and from d-glucosazone. It crystallizes with great difficulty, fuses at 95°, is very soluble in water, and insoluble in absolute alcohol. Although called d-fructose, because of its formation from d-glucosazone, it is strongly lævorotary: $[a]_D=-71.4°$. It is less readily fermentable than glucose, which it equals in the readiness with which it reduces cupropotassic solutions. With phenylhydrazin it yields d-glucosazone (p. 430).

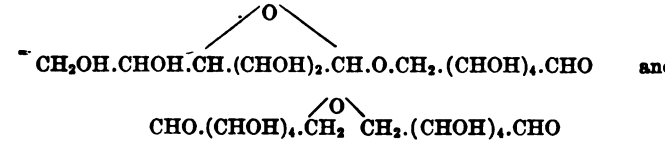
**Sorbinose,** also a ketohexose, occurs in the berries of the mountain ash. It does not ferment. Its osazone fuses at 164°.

### DISACCHARIDS—SACCHAROBIOSES.

Disaccharids consist of two molecules of monosaccharids, united with elimination of $H_2O$. So far as is known they are all derived from the hexoses, and their formula is consequently $C_{12}H_{22}O_{11}$. They are all capable of yielding two hexose molecules by hydrolysis: $C_{12}H_{22}O_{11}+H_2O=2C_6H_{12}O_6$, a change which is called "inversion." The union of the two monosaccharid molecules is either through the aldehyde, ketone, or alcoholic groups. Of the three most important disaccharids, saccharose, lactose and maltose, the first named has no reducing power, and yields no osazone with phenylhydrazin. It therefore contains no aldehyde or ketone group. When heated with acetic anhydrid to 160° it forms an octacetyl ester, $C_{12}H_{14}O_3(O.C_2H_3O)_8$. It therefore contains eight hydroxyls. When hydrolyzed it yields d-glucose and d-fructose (laevogyratory). From the above facts we may infer that saccharose is derived from the two hexoses named, united through the aldehyde and ketone groups, a constitution which may be represented by the formulæ:




Lactose and maltose both cause reduction and yield osazones. On hydrolysis the former yields d-glucose and galactose, and the latter only d-glucose. They each consequently retain an aldehyde (or ketone) group, and their constitution may probably be represented thus:




The disaccharids are hydrolyzed by boiling with very dilute acids, or even with water, and by several enzymes such as diastase, emulsin, invertin, ptyalin, trypsin and pepsin.

**Saccharose—Cane Sugar**—exists in many roots, fruits and grasses, and is produced from the sugar-cane, *Saccharum officinarum*, sorghum, *Sorghum saccharatum*, beet, *Beta vulgaris*, and sugar-maple, *Acer saccharinum*.

For the extraction of sugar the expressed juice is heated in large pans to about 100° (212° F.); milk of lime is added, which causes

the precipitation of albumen, wax, calcic phosphate, etc.; the clear liquid is drawn off, and "delimed" by passing a current of $CO_2$ through it; the clear liquid is again drawn off and evaporated, during agitation, to the crystallizing point; the product is drained, leaving what is termed **raw or muscovado sugar**, while the liquor which drains off is **molasses.** The sugar so obtained is purified by the process of "refining," which consists essentially in adding to the raw sugar, in solution, albumen in some form, which is then coagulated; filtering first through canvas, afterward through animal charcoal; and evaporating the clear liquid in "vacuum-pans," at a temperature not exceeding 72° (161.6° F.), to the crystallizing point. The product is allowed to crystallize in earthen moulds; a saturated solution of pure sugar is poured upon the crystalline mass in order to displace the uncrystallizable sugar which still remains, and the loaf is finally dried in an oven. The liquid displaced as above is what is known as **sugar-house syrup.**

Pure sugar should be entirely soluble in water; the solution should not turn brown when warmed with dilute potassium hydroxid solution; should not reduce Fehling's solution, and should give no precipitate with ammonium oxalate.

**Beet-sugar** is the same as cane-sugar, except that, as usually met with in commerce, it is lighter, bulk for bulk. **Sugar-candy**, or **rock-candy**, is cane-sugar allowed to crystallize slowly from a concentrated solution, without agitation. **Maple-sugar** is a partially refined, but not decolorized variety of cane-sugar.

Saccharose crystallizes in small, white, monoclinic prisms; or, as sugar-candy, in large, yellowish, transparent crystals; sp. gr. 1,606. It is very soluble in water, dissolving in about one-third its weight of cold water, and more abundantly in hot water. It is insoluble in absolute alcohol or ether, and its solubility in water is progressively diminished by the addition of alcohol. Aqueous solutions of cane-sugar are dextrogyrous, $[a]_D = +66.5°$.

When saccharose is heated to 160° (320° F.) it fuses, and the liquid, on cooling, solidifies to a yellow, transparent, amorphous mass, known as **barley-sugar**; at a slightly higher temperature, it is decomposed into glucose and lævulosan; at a still higher temperature, $H_2O$ is given off, and the glucose already formed is converted into glucosan; at about 200° (392° F.) the evolution of $H_2O$ is more abundant, and there remains a brown material known as **caramel**, or **burnt sugar**; a tasteless substance, insoluble in strong alcohol, but soluble in $H_2O$, or in aqueous alcohol, and used to communicate color to spirits; finally, at higher temperatures, methyl hydrid and the two oxids of carbon are given off; a brown oil, acetone, acetic acid, and aldehyde distil over; and a carbonaceous residue remains.

If saccharose be boiled for some time with $H_2O$, it is converted into inverted sugar, which is a mixture of glucose and fructose: $C_{12}H_{22}O_{11}+H_2O=C_6H_{12}O_6+C_6H_{12}O_6$. With a solution of saccharose the polarization is dextrogyrous, but, after inversion, it becomes lævogyrous, because the left-handed action of the molecule of fructose produced, $[a]_D=-71.4°$, is only partly neutralized by the right-handed action of the glucose, $[a]_D=+52.6°$. This inversion of cane sugar is utilized in the testing of samples of sugar. On the other hand, it is to avoid its occurrence, and the consequent loss of sugar, that the vacuum-pan is used in refining—its object being to remove the $H_2O$ at a low temperature.

With potassium chlorate, sugar forms a mixture which detonates when subjected to shock, and which deflagrates when moistened with $H_2SO_4$. Concentrated $H_2SO_4$ blackens it. Dilute $HNO_3$, when heated with saccharose, oxidizes it to saccharic and oxalic acids.

When moderately heated with liquor potassæ, cane-sugar does not turn brown, as does glucose; but by long ebullition it is decomposed by the alkalies, much less readily than glucose, with formation of acids of the fatty series and oxalic acid.

With the bases, saccharose forms definite compounds called **sucrates** (improperly saccharates, a name belonging to the salts of saccharic acid). With Ca it forms five compounds. Calcium hydroxid dissolves readily in solutions of sugar, with formation of a Ca compound, soluble in $H_2O$, containing an excess of sugar.

During the process of digestion, probably in the small intestine, cane-sugar is converted into glucose.

**Lactose—Milk Sugar**—*Lactine*—**Saccharum lactis** (U. S., Br.)—occurs in the milk of the mammalia, in the amniotic fluid of cows, and in the urine of women towards the end of gestation and during lactation. It may be obtained from skim-milk by coagulating the casein with a small quantity of $H_2SO_4$, filtering, evaporating, redissolving, decolorizing with animal charcoal, and recrystallizing.

It forms prismatic crystals; sp. gr. 1.53; hard, transparent, faintly sweet, soluble in 6 parts of cold and 2.5 parts of boiling $H_2O$; soluble in acetic acid; insoluble in alcohol and in ether. Its solutions are dextrogyrous $[a]_D=+52.5°$. The crystals, dried at 100° (212° F.), contain 1Aq, which they lose at 150° (302° F.).

Lactose is not altered by contact with air. Heated with dilute mineral acids or with strong organic acids, it is converted into galactose. $HNO_3$ oxidizes it to mucic and oxalic acids. A mixture of $HNO_3$ and $H_2SO_4$ converts it into an explosive nitro-compound. With organic acids it forms esters. With soda, potash and lime it forms compounds similar to those of saccharose, from which lactose may be recovered by neutralization, unless they have been heated to 100°

(212° F.), at which temperature they are decomposed. It reduces Fehling's solution, and reacts with Trommer's test. Its osazone fuses at 200° (392° F.).

In the presence of yeast, lactose is capable of alcoholic fermentation, which takes place slowly, and, as it appears, without previous transformation of the lactose into either glucose or galactose. On contact with putrefying proteins it enters into lactic fermentation.

The average proportion of lactose in different milks is as follows: Cow, 5.5 per cent.; mare, 5.5; ass, 5.8; human, 5.3; sheep, 4.2; goat, 4.0. It is converted into galactose by the pancreatic secretion.

**Maltose**—is formed, along with dextrins, during the conversion of starch, or of glycogen, into sugar by the action of diastase (in malting grain), and of the enzymes of the saliva and the pancreatic juice. It is also an intermediate product in the hydrolysis of starch by dilute sulfuric acid. Maltose crystallizes in hard, white needles aggregated into crusts. It is less soluble in alcohol than is glucose, and has a much higher dextrogyratory power $[a]_D = +137°$. It reduces Fehling's solution. It is hydrolyzed by boiling with dilute acids, yielding only d-glucose. It is fermentable. Its osazone fuses as 206°. Nitric acid oxidizes it to d-saccharic acid.

**Isomaltose**—*Gallisin*—is formed along with maltose, in the action of diastase, saliva, or pancreatic juice, or of boiling dilute acids, on starch, and exists in beer and artificial glucose. It is also formed by the prolonged action of strong HCl on d-glucose. It is very soluble in water, very sweet, and does not ferment, or does so very slowly. Its osazone forms yellow needles, which fuse at 150° (302° F.), and are rather soluble in hot water.

### TRISACCHARIDS.

Several members of this group have been obtained from different vegetables. They have the formula $C_{18}H_{32}O_{16}$. The best known are **Raffinose**, or **Melitose**, which occurs in eucalyptus-manna, in cotton seed, and in beet-sugar molasses; and **Melecitose**, from the manna of *Pinus larix*.

### POLYSACCHARIDS.

The starches, gums, and celluloses, which form this class, have the empirical formula $C_6H_{10}O_5$, but their molecular weights are much greater than that represented by that formula. They are very widely distributed in vegetable nature. On hydrolysis they are finally decomposed to monosaccharids, for the most part hexoses, although some of the gums yield pentoses.

**Starch—Amylum**—the most important member of the group, exists in the roots, stems, and seeds of all plants, and is obtained commercially from rice, potatoes, and maize. It is a white powder, consisting of granules which are round, ovoid or irregular in outline, and in some cases marked with a central spot or line, called the hilum, and with concentric rings. Differences in the shape, size and markings of the granules are utilized to identify the vegetable from

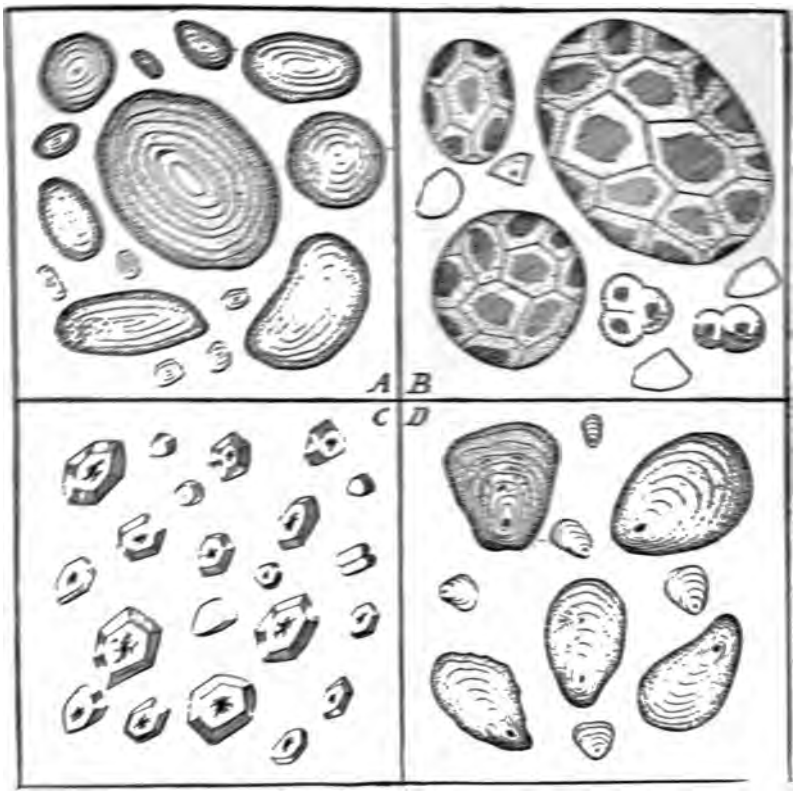



*Fig. 34.* *A*, wheat-starch; *B*, oat-starch; *C*, maize-starch; *D*, potato-starch. × 300 diameters.

which the starch was obtained. Some of the commoner forms are shown in *Fig. 35*. Air-dried starch contains 18% of water, of which it loses 8% in vacuo, and the remainder only at 145° (293° F.). Starch is insoluble in cold water and in alcohol. If 15 to 20 parts of $H_2O$ be gradually heated with one part of starch, the granules swell at about 55° (131° F.), and at 80° (176° F.) they have lost their structure, have swelled to thirty times their original volume, and have formed a homogeneous, translucent, gelatinous mass, commonly known as **starch paste**. This hydrated starch consists of an

insoluble portion, **starch cellulose**, and a soluble portion, **granulose**, or **soluble starch.** Granulose forms an opalescent solution in water, from which it is precipitated as a white powder by alcohol. Its solutions are strongly dextogyrous, $[a]_D = +207°$ (about). By prolonged boiling with water, or, more rapidly, by boiling dilute mineral acids, or by the action of diastatic enzymes, soluble starch is converted into dextrins, maltose, and finally, d-glucose. Dry heat causes the starch granules to burst, with formation of dextrin. A dilute solution of iodin produces a violet-blue color with starch, whether dry, hydrated, or in solution. The color is discharged by heat, but reappears on cooling. Concentrated $HNO_3$ dissolves starch in the cold, forming a nitro-product, called **xylodin**, or **pyroxam**, which is insoluble in water, soluble in a mixture of alcohol and ether, and explosive.

**Glycogen—Animal Starch**—occurs in the liver, the placenta, white blood corpuscles, pus cells, young cartilage cells, muscular tissue and many embryonic tissues, also in many molluscs. It is best obtained from liver tissue, by extraction with hot water and precipitation by alcohol, after separation of protein bodies by potassium iodhydrargyrate and acetic acid. It is a snow-white, floury powder, amorphous, tasteless, and odorless; soluble in water, forming an opalescent solution, insoluble in alcohol or ether. Its solutions are strongly dextrogyrous, $[a]_D = +196.6°$. Glycogen is converted into dextrins, maltose, and, ultimately, d-glucose by the action of boiling dilute acids, and by the salivary, pancreatic and hepatic diastatic enzymes. Glycogen is colored wine-red by iodin, the color being discharged by heat and returning on cooling. Its solutions dissolve, but do not reduce cupric hydroxid.

Other starches are: **Paramylum**, occurring in certain infusoria; **Lichenin**, in lichens and mosses; and **Inulin**, in the roots of dahlia, chicory and other plants.

**Gums**—are amorphous, translucent substances occurring in many plants. They are insoluble in alcohol and in ether. With water some of them, the **true gums**, form clear solutions; while others, the **vegatable mucilages**, swell up to sticky masses which cannot be filtered through paper. On boiling with dilute $H_2SO_4$ the gums yield d-glucose, galactose, or l-arabinose. Nitric acid oxidizes them to mucic, oxalic and saccharic acids.

The commoner members of the group are: **Arabin**, the chief constituent of gum arabic (acacia) and gum senegal; and **Bassorin**, the chief ingredient of gum tragacanth, Bassora gum, and plum and cherry gums.

**Dextrin**—*British gum*—a substance resembling gum arabic in appearance and in many properties, is obtained by one of three methods: (1) by subjecting starch to a dry heat of 175° (347° F.);

(2) by heating starch with dilute $H_2SO_4$ to 90° (194° F.) until a drop of the liquid gives only a wine-red color with iodin; neutralizing with chalk, filtering, concentrating, precipitating with alcohol; (3) by the action of diastase (infusion of malt) upon hydrated starch. As soon as the starch is dissolved the liquid must be rapidly heated to boiling to prevent saccharification.

Commercial dextrin is a colorless, or yellowish, amorphous powder, soluble in $H_2O$ in all proportions, forming mucilaginous liquids. When obtained by evaporation of its solution, it forms masses resembling gum arabic in appearance. Its solutions are dextrogyrous, and reduce cupro-potassic solutions under the influence of heat, to amounts varying with the method of formation of the sample. It is colored wine-red by iodin. It is extensively used as a substitute for gum acacia.

By the action of diastase upon starch, four dextrins are produced: (1) Erythrodextrin, which is colored red by iodin, and which is easily attacked by diastase; (2) Achroödextrin $\alpha$, not colored by iodin; partially converted into sugar by diastase; rotary power $[a]_D = +210°$; reducing power (glucose=100)=12; (3) Achroödextrin $\beta$, not colored by iodin, nor decomposable in twenty-four hours by diastase; rotary power + 190°; reducing power=12; (4) Achroödextrin $\gamma$, not colored by iodin, nor decomposed by diastase; slowly converted into glucose by dilute $H_2SO_4$; rotary power = +150°; reducing power=28.

An explanation of this series of transformations has been suggested in the supposition that the molecule of starch consists of $50(C_{12}H_{20}O_{10})$; that this is first converted into soluble starch $10(C_{12}H_{20}O_{10})$; and that this is then converted into the different forms of dextrin by a series of hydrations attended by simultaneous formation of maltose, of which the final result might be represented by the equation:

$$\underset{\text{Soluble starch.}}{10(C_{12}H_{20}O_{10})} + \underset{\text{Water.}}{8(H_2O)} = \underset{\text{Achroödextrin.}}{2(C_{12}H_{20}O_{10})} + \underset{\text{Maltose.}}{8(C_{12}H_{22}O_{11})}$$

Cellulose—*Cellulin*—forms the basis of all vegetable tissues. It exists, almost pure, in the pith of elder and of other plants, in the purer, unsized papers, in cotton, and in the silky appendages of certain seeds. Cotton, freed from extraneous matter by boiling with KHO and afterwards with dilute HCl, yields pure cellulose (absorbent cotton). It is white, has the shape of the fiber from which it was derived, is insoluble in the usual solvents, but soluble in the dark blue liquid formed by dissolving copper in ammonia in contact with air.

Vegetable parchment—Parchment paper—is obtained by dipping unsized paper for an instant in $H_2SO_4$, diluted with an equal

volume of $H_2O$, washing thoroughly, and drying. It is a tough material resembling animal parchment.

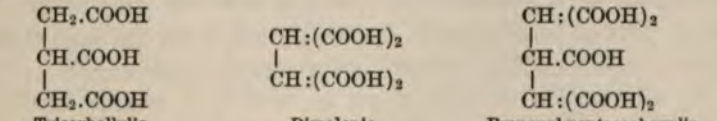
**Gun-cotton—Pyroxylin**—is obtained by dipping pure cotton in a cold mixture of one part of $HNO_3$ and two-thirds of $H_2SO_4$ for from three to ten minutes, washing thoroughly, and drying. It consists of hexanitrocellulose, $C_{12}H_{14}(O.NO_2)_6O_4$, is violently explosive, and is insoluble in a mixture of alcohol and ether.

**Soluble pyroxylin**—is obtained by acting on cotton with a warm mixture of twenty parts of nitre and thirty parts of concentrated $H_2SO_4$, washing and drying. It consists of penta- and tetra-nitrocellulose, is soluble in a mixture of alcohol and ether, and is used in the preparation of collodion. **Explosive gelatin**, or **smokeless powder**, is produced by dissolving nitro-glycerol in an equal part of collodion. **Celluloid** is a mixture of gun-cotton and camphor, combined by pressure.

## CARBOXYLIC ACIDS.

These compounds are the fourth products of oxidation of the paraffins (p. 238), and contain the characterizing group of atoms O:C.OH (carboxyl). They are either pure acids, containing only the carboxyl and hydrocarbon groups; or alcohol-acids, containing also the groups $CH_2OH$, CHOH or COH; or aldehyde-acids, containing CHO; or ketone-acids, containing CO; or of still more complex function, containing two or more of the above groups.

The most important of the pure acids are those of the acetic ($C_nH_{2n}O_2$), and oxalic ($C_nH_{2n-2}O_4$) series, the former of which are monobasic, the latter dibasic. Other pure acids of higher basicity are also known in which the carboxyl groups are substituted for hydrogen atoms in the hydrocarbon. The following are examples of such acids:




Tricarballylic acid. Dimalonic acid. Propenyl-pentacarboxylic acid.

### PARAFFIN MONOCARBOXYLIC ACIDS—VOLATILE FATTY ACIDS—ACETIC SERIES—SERIES $C_nH_{2n}O_2$

The lowest terms of the series are volatile liquids, the highest are solids and exist in their glycerol esters in the fats; hence the name of **volatile fatty acids**. The solid acids, the tenth and higher of the series, cannot be distilled without decomposition except in superheated steam.

It is a colorless liquid, having an acid taste and a penetrating odor; it acts as a vesicant; it boils at 100° (212° F.), and, when pure, crystallizes at 0° (32° F.). It is miscible with $H_2O$ in all proportions.

The mineral acids decompose it into $H_2O$ and carbon monoxid. Oxidizing agents convert it into $H_2O$ and carbon dioxid. Alkaline hydroxids decompose it with formation of a carbonate and liberation of H. It acts as a reducing agent with the salts of the noble metals.

**Acetic Acid**—*Acetyl hydroxid—Hydrogen acetate — Pyroligneous acid*—**Acidum aceticum** (U. S.; Br.)—$CH_3.COOH$—60.

It is formed—(1) By the oxidation of alcohol: $CH_3.CH_2OH + O_2 = CH_3.COOH + H_2O$.

(2) By the dry distillation of wood.

(3) By the decomposition of natural acetates by mineral acids.

(4) By the action of potash in fusion on sugar, starch, oxalic, tartaric, citric acids, etc.

(5) By the decomposition of gelatin, fibrin, casein, etc., by $H_2SO_4$ and manganese dioxid.

(6) By the action of carbon dioxid upon sodium methyl: $CO_2 + NaCH_3 + C_2H_3O_2Na$; and decomposition of the sodium acetate so produced.

The acetic acid used in the arts and in pharmacy is prepared by the destructive distillation of wood. The products of the distillation, which vary with the nature of the wood used, are numerous. Charcoal remains in the retort, while the distilled product consists of an acid, watery liquid; a tarry material; and gaseous products. The gases are carbon dioxid, carbon monoxid, and hydrocarbons. The tar is a mixture of empyreumatic oils, hydrocarbons, phenols, acetic acid, ammonium acetate, etc.

The acid liquid is very complex, and contains, besides acetic acid, formic, propionic, butyric, valerianic, and oxyphenic acids, acetone, naphthalene, benzene, toluene, cumene, creasote, methyl alcohol, methyl acetate, etc. Partially freed from tar by decantation, it still contains about 20 per cent. of tarry and oily material, and about 4 per cent. of acetic acid; this is the crude **pyroligneous acid** of commerce.

The crude product is subjected to a first purification by distillation; the first portions are collected separately and yield methyl alcohol (p. 241); the remainder of the distillate is the *distilled pyroligneous acid*, used to a limited extent as an antiseptic, but principally for the manufacture of acetic acid and the acetates. Crude pyroligneous acid is purified by conversion into sodium acetate, which, after calcination, is decomposed by $H_2SO_4$, and the liberated acetic

[redacted]

*Vinegar* is a sour liquid containing acetic acid and [redacted] It is obtained from [redacted] containing 10 per cent. or less of alcohol, [redacted] by the transforming of atmospheric oxygen into acetic acid during the process of formation of a peculiar vegetable ferment, *mycoderma aceti*, or popularly, as *mother of vinegar*. The liquids from which vinegar is made are wine, cider, and [redacted] alcohol, obtained by fermenting artificial glucose, is frequently added; the most esteemed being that obtained from white wine. *Wine vinegar* has a pleasant, acid taste and odor; it consists of water, acetic acid (about 5 per cent.), potassium bitar-

trate, alcohol, acetic ether, glucose, malic acid, mineral salts present in wine, a fermentable, nitrogenized substance, coloring matter, etc. Sp. gr. 1.020 to 1.025. When evaporated it yields from 1.7 to 2.4 per cent. of solid residue. Vinegars made from alcoholic liquids other than wine contain no potassium bitartrate, contain less acetic acid, and have not the aromatic odor of wine vinegar. *Cider vinegar* is of sp. gr. 1.020; is yellowish, has an odor of apples, and yields 1.5 per cent. of extract on evaporation. *Beer vinegar* is of sp. gr. 1.032; has a bitterish flavor and an odor of sour beer; it leaves 6 per cent. of extract on evaporation. Two parts of good wine vinegar neutralize 10 parts of sodium carbonate; the same quantity of cider vinegar, 3.5 parts; and of beer vinegar, 2.5 parts of carbonate.

**Distilled vinegar** is prepared by distilling vinegar in glass vessels; it contains none of the fixed ingredients of vinegar, but its volatile constituents (acetic acid, water, alcohol, acetic ether, odorous principles, etc.), and a small quantity of aldehyde.

When dry cupric acetate is distilled, a blue, strongly acid liquid passes over; this, upon rectification, yields a colorless, mobile liquid, which boils at 56° (132.8° F.), has a peculiar odor, and is a mixture of acetic acid, water, and acetone, known as **radical vinegar.**

**Toxicology.**—When taken internally, acetic acid and vinegar (the latter in doses of 100 to 150 cc.) act as irritants and corrosives, causing in some instances perforation of the stomach, and death in 6–15 hours. Milk of magnesia should be given as an antidote, with a view to neutralizing the acid.

**Propionic Acid**—$CH_3.CH_2.COOH$—is formed by the action of caustic potash upon sugar, starch, gum, and ethyl cyanid; during fermentation, vinous or acetic; in the distillation of wood; during the putrefaction of peas, beans, etc.; by the oxidation of normal propylic alcohol, etc. It is best prepared by heating ethyl cyanid with potash until the odor of the ester has disappeared; the acid is then liberated from its potassium compound by $H_2SO_4$ and purified.

It is a colorless liquid, sp. gr. 0.996, solidifies at —36.5° (—33.7° F.), boils at 140° (284° F.), mixes with water and alcohol in all proportions, resembles acetic acid in odor and taste. Its salts are soluble and crystallizable.

**Butyric Acid—Propyl-formic acid**—$CH_3.CH_2.CH_2.COOH$—has been found in the milk, perspiration, muscular fluid, the juices of the spleen and of other glands, the urine, contents of the stomach and large intestines, fæces, and guano; in certain fruits, in yeast, in the products of decomposition of many vegetable substances; and in natural waters; in fresh butter in small quantity, more abundantly in that which is rancid.

It is formed by the action of $H_2SO_4$ and manganese dioxid, aided

by heat, upon cheese, starch, gelatin, etc.; during the combustion of tobacco (as ammonium butyrate); by the action of $HNO_2$ upon oleic acid; during the putrefaction of fibrin and other proteins; during a peculiar fermentation of glucose and starchy material in the presence of casein or gluten. This fermentation, known as the butyric, takes place in two stages; at first the glucose is converted into lactic acid: $C_6H_{12}O_6=2(C_2H_6O_3)$; and this in turn is decomposed into butyric acid, carbon dioxid, and hydrogen: $2C_2H_6O_3=C_4H_8O_2+2CO_2+2H_2$.

Butyric acid is obtained from the animal charcoal which has been used in the purification of glycerol, in which it exists as calcium butyrate. It is also formed by subjecting to fermentation a mixture composed of glucose, water, chalk, and cheese or gluten. The calcium butyrate is decomposed by $H_2SO_4$, and the butyric acid is separated by distillation.

Butyric acid is a colorless, mobile liquid, having a disagreeable, persistent odor of rancid butter, and a sharp, acid taste; soluble in water, alcohol, ether, and methyl alcohol; boils at 164° (327.2° F.), distilling unchanged; solidifies in a mixture of solid carbon dioxid and ether; sp. gr. 0.974 at 15° (59° F.); a good solvent of fats.

It is not acted upon by $H_2SO_4$ in the cold, and only slightly under the influence of heat. Nitric acid dissolves it unaltered in the cold, but on the application of heat, oxidizes it to succinic acid. Dry Cl under the influence of sunlight, and Br under the influence of heat and pressure, form products of substitution with butyric acid. It readily forms esters and salts.

Butyric acid is formed in the intestine, by the process of fermentation mentioned above, at the expense of those portions of the carbohydrate elements of food which escape absorption, and is discharged with the fæces as ammonium butyrate.

**Isobutyric Acid**—**Isopropyl-formic acid**—$\frac{CH_3}{CH_3}\!\!>\!CH.COOH$—boils at 155° (311° F.), has been found in human fæces. It corresponds to isobutyl alcohol, from which it is produced by oxidation.

**Valerianic Acids**—$C_4H_9.COOH$—102.—Corresponding to the four primary amylic alcohols, there are four possible amylic or valerianic acids:

**Normal Valerianic Acid**—**Butyl-formic acid**—*Propyl-acetic acid*—is obtained by the oxidation of normal amylic alcohol. It is an oily liquid, boils at 185° (365° F.), and has an odor resembling that of butyric acid.

**Ordinary Valerianic Acid**—*Delphinic acid*—*Phocenic acid*—**Isovaleric acid**—*Isopropyl-acetic acid*—**Isobutyl-formic acid**—**Acidum valerianicum** (Br.).—This acid exists in the oil of the porpoise, and in valerian root and in angelica root. It is formed during putrid fermentation or oxidation of proteins. It occurs in the urine and

fæces in typhus, variola, and acute atrophy of the liver. It is also formed in a variety of chemical reactions, and notably by the oxidation of amylic alcohol.

The ordinary valerianic acid is an oily, colorless liquid, having an odor of old cheese, and a sharp, acrid taste. It solidifies at —51° (—59.8° F.); boils at 173°–175° (343.4°–347° F.); sp. gr. 0.9343–0.9465 at 20° (68° F.); burns with a white, smoky flame. It dissolves in 30 parts of water, and in alcohol and ether in all proportions. It dissolves phosphorus, camphor and certain resins.

**Methyl-ethyl-acetic Acid**—boils at 175° (347° F.). It contains an asymmetric carbon atom and exists in two optically opposed modifications (p. 265).

**Trimethyl-acetic Acid**—*Pivalic acid*—is a crystalline solid, which fuses at 35.5° (96° F.) and boils at 163.7° (326.7° F.); sparingly soluble in $H_2O$; obtained by the action of mercuric cyanid upon tertiary butyl iodid.

**Caproic Acids**—*Hexylic acids*—$C_5H_{11}.COOH$ — 116.—There exist seven isomeres having the composition indicated above, some of which have been prepared from butter, cocoa-oil and cheese, and by decomposition of amyl cyanid, or by oxidation of hexyl alcohol.

The acid obtained from butter, in which it exists as a glyceric ester, is a colorless, oily liquid, boils at 205° (401° F.); sp. gr. 0.931 at 15° (59° F.); has an odor of perspiration and a sharp, acid taste; is very sparingly soluble in water, but soluble in alcohol. It is the normal hexylic acid: $CH_3.(CH_2)_4.COOH$.

**Œnanthylic Acid**—*Heptylic acid*—$C_6H_{13}.COOH$—130—exists in spirits distilled from rice and maize, and is formed by the action of $HNO_3$ on fatty substances, especially castor-oil. It is a colorless oil; sp. gr. 0.9167; boils at 212° (413.6° F.).

**Caprylic Acid**—*Octylic acid*—$C_7H_{15}.COOH$—144—accompanies caproic acid in butter, cocoa-oil, etc. It is a solid; fuses at 15° (59° F.); boils at 236° (457° F.); almost insoluble in $H_2O$.

**Pelargonic Acid**—*Nonylic acid*—$C_8H_{17}.COOH$—158.—A colorless oil, solid below 10° (50° F.); boils at 260° (500° F.); exists in oil of geranium, and is formed by the action of $HNO_3$ on oil of rue.

**Capric Acid**—*Decylic Acid*—$C_9H_{19}.COOH$—172—exists in butter, cocoa-oil, etc., associated with caproic and caprylic acids in their glyceric esters, and in the residues of distillation of Scotch whisky, as amyl caprate. It is a white, crystalline solid; melts at 27.5° (81.5° F.); boils at 273° (523.4° F.).

**Lauric Acid**—*Laurostearic acid*—$C_{11}H_{23}.COOH$—200—is a solid, fusible at 43.5° (110.3° F.); obtained from laurel berries, cocoa-butter and other vegetable fats.

**Myristic Acid**—$C_{13}H_{27}.COOH$—228.—A crystalline solid, fusible

at 54° (129.2° F.); existing in many vegetable oils, cow's butter and spermaceti.

**Palmitic Acid**—*Ethalic acid*—$C_{15}H_{31}.COOH$—256—exists in palm-oil, in combination when the oil is fresh, and free when the oil is old; it also enters into the composition of nearly all animal and vegetable fats. It is obtained from the fats, palm-oil, etc., by saponification with caustic potash and subsequent decomposition of the soap by a strong acid. It is also formed by the action of caustic potash in fusion upon cetyl alcohol (ethal), and by the action of the same reagent upon oleic acid.

Palmitic acid is a white, crystalline solid; odorless, tasteless; lighter than $H_2O$, in which it is insoluble; quite soluble in alcohol and in ether; fuses at 62° (143.6° F.); distils unchanged with vapor of water.

**Margaric Acid**—$C_{16}H_{33}.COOH$—270—formerly supposed to exist as a glycerid in all fats, solid and liquid. What had been taken for margaric acid was a mixture of 90 per cent. of palmitic and 10 per cent. of stearic acid. It is obtained by the action of potassium hydroxid upon cetyl cyanid, as a white, crystalline body; fusible at 59.9° (140° F.).

**Stearic Acid**—$C_{17}H_{35}.COOH$—284—exists as a glycerid in all solid fats and in many oils, and also free to a limited extent.

To obtain it pure the fat is saponified with an alkali, and the soap decomposed by HCl; the mixture of fatty acids is dissolved in a large quantity of alcohol, and the boiling solution *partly* precipitated by the addition of a concentrated solution of barium acetate. The precipitate is collected, washed and decomposed by HCl; the stearic acid which separates is washed and recrystallized from alcohol. The process is repeated until the product fuses at 70° (158° F.). Stearic acid is formed from oleic acid (p. 374) by the action of iodin under pressure at 270°–280° (518°–536° F.).

Pure stearic acid is a colorless, odorless, tasteless solid; fusible at 70° (158° F.); unctuous to the touch; insoluble in $H_2O$, very soluble in alcohol and in ether. The alkaline stearates are soluble in $H_2O$; those of Ca, Ba, and Pb are insoluble.

Stearic and palmitic acids exist free in the intestine during the digestion of fats, a portion of which is decomposed by the action of the pancreatic secretion into fatty acids and glycerol. The same decomposition also occurs in the presence of putrefying proteins.

**Arachic Acid**—$C_{19}H_{39}.COOH$—312—exists as a glycerid in peanut oil (now largely used as a substitute for olive oil), in oil of ben, and in small quantity in butter. It is a crystalline solid, which melts at 75° (167° F.).

PARAFFIN DICARBOXYLIC ACIDS —OXALIC SERIES— $C_nH_{2n-2}O_4$.

These acids are derivable from the paraffins by oxidation of two $CH_3$ groups, or from the diprimary alcohols by oxidation of the $CH_2OH$ groups (pp. 238, 251). They contain two carboxyl groups and are therefore dibasic. But one acid is possibly derivable from ethane (oxalic acid), and from propane (malonic acid). From the two butanes two acids are derivable; from the three pentanes four acids, and from the five hexanes nine acids; all of which are known. The molecular structure of the acids derivable from the butanes and pentanes are shown in the following formulæ:

$CH_3.CH_2.CH_2.CH_3$ — Butane.

$CH_3(CH_3)CH.CH_3$ — Isobutane.

$COOH.CH_2.CH_2.COOH$ — Succinic acid.

$COOH(CH_3)CH.COOH$ — Isosuccinic acid.

$CH_3.CH_2.CH_2.CH_2.CH_3$ — Normal Pentane.

$(CH_3)_2:CH.CH_2.CH_3$ — Dimethyl-ethyl Methane.

$(CH_3)_4::C$ — Tetramethyl Methane.

$COOH.(CH_2)_3.COOH$ — Glutaric Acid.

$(COOH)_2:CH.CH_2.CH_3$ — Ethyl-malonic Acid.

$(COOH)_2:C:(CH_3)_2$ — Dimethyl-malonic Acid.

$COOH(CH_3)CH.CH_2.COOH$ — Methyl-succinic Acid.

The acids of this series may be obtained: (1) By the oxidation of the corresponding diprimary alcohols (p. 251), dialdehydes (p. 261), primary oxyaldehydes (p. 263), primary oxyacids (p. 289), aldehyde acids (p. 297), paraffin monocarboxylic acids (p. 277), olefin monocarboxylic acids (p. 373), or paraffins (p. 238).

(2) By the reduction of the olefin dicarboxylic acids (p. 375).

(3) By the action of silver upon the monoiodo or monobromo fatty acids: $2BrCH_2.COOH+2Ag=2AgBr+COOH.CH_2.CH_2.COOH$.

(4) By the action of acids or alkalies upon the cyano fatty acids: $CN.CH_2.COOH+2H_2O=NH_3+COOH.CH_2.COOH$; or upon the dicyanids: $CN.CH_2.CH_2.CN+4H_2O=2NH_3+COOH.CH_2.CH_2.COOH$. (p. 278).

The action of heat upon these acids and their salts differs according to the attachment of the carboxyl groups. (1) Oxalic acid and acids in which the two carboxyls are attached to the same carbon atom are either decomposed into the two oxids of carbon and water: $COOH.COOH=CO_2+CO+H_2O$; or into carbon dioxid and a fatty acid: $COOH.COOH=CO_2+H.COOH$.

(2) When the two carboxyls are attached to neighboring carbon atoms the acids are decomposed into water and an anhydrid (p. 310):

$COOH.CH_2.CH_2.COOH = H_2O + \begin{matrix} CH_2.CO \\ | \\ CH_2.CO \end{matrix} O$ . 3). When the carboxyls are attached to remote carbon atoms their calcium salts are converted by heat into cyclic ketones and carbonate: $CH_2 \begin{matrix} CH_2.CH_2.CO_2 \\ CH_2.CH_2.CO_2 \end{matrix} Ca = CaCO_3 + CH_2 \begin{matrix} CH_2.CH_2 \\ CH_2.CH_2 \end{matrix} CO$.

**Oxalic Acid**—$COOH.COOH$—90—$C_2H_4O_2,2Aq$—126—does not occur free in nature, but in the oxalates of K, Na, Ca, Mg, and Fe in the juices of many plants: sorrel, rhubarb, cinchona, oak, etc.; as a native ferrous oxalate; and in small quantity in human urine. It is prepared artificially by oxidizing sugar or starch by $HNO_3$, or by the action of an alkaline hydroxid in fusion upon sawdust. The soluble alkaline oxalate obtained by the latter method is converted into the insoluble Ca or Pb salt, which is washed and decomposed by an equivalent quantity of $H_2SO_4$ or $H_2S$; and the liberated acid purified by recrystallization.

Oxalic acid is also formed by the oxidation of many organic substances: alcohol, glycol, sugar, etc.; by the action of potash in fusion upon the alkaline formates; and by the action of K or Na upon $CO_2$.

It crystallizes in transparent prisms, containing 2 Aq, which effloresce on exposure to air, and lose their Aq slowly but completely at 100° (212° F.), or in a dry vacuum. It fuses at 98° (208.4° F.) in its Aq; at 110°–132° (230°-269.6° F.) it sublimes in the anhydrous form, while a portion is decomposed; above 160° (320° F.) the decomposition is more extensive; $H_2O$, $CO_2$, CO, and formic acid are produced, while a portion of the acid is sublimed unchanged. It dissolves in 15.5 parts of water at 10° (50° F.); the presence of $HNO_3$ increases its solubility. It is quite soluble in alcohol. It has a sharp taste and an acid reaction in solution.

Oxalic acid is readily oxidized; in watery solution it is converted into $CO_2$ and $H_2O$, slowly by simple exposure to air, more rapidly in the presence of platinum-black or of the salts of platinum and gold, under the influence of sunlight, or when heated with $HNO_3$, manganese dioxid, chromic acid, Br, Cl, or hypochlorous acid. Its oxidation, when it is triturated dry with lead dioxid, is sufficiently active to heat the mass to redness. $H_2SO_4$, $H_3PO_4$ and other dehydrating agents decompose it into $H_2O$, CO and $CO_2$.

**Analytical Characters.**—(1) In neutral or alkaline solution: a white ppt. with a solution of Ca salt. (2) Silver nitrate: a white ppt., soluble in $HNO_3$, and in $NH_4HO$. The ppt. does not darken when the fluid is boiled, but when dried and heated on platinum foil, it explodes. (3) Lead acetate, in solutions not too dilute: a white ppt., soluble in $HNO_3$, insoluble in acetic acid.

**Toxicology.**—Although certain oxalates are constant constituents of vegetable food and of the human body, the acid itself, as well as monopotassic oxalate, is a violent poison when taken internally, acting both locally as a corrosive upon the tissues with which it comes in contact and as a true poison, the predominance of either action depending upon the concentration of the solution. Dilute solutions may produce death without pain or vomiting, and after symptoms resembling those of narcotic poisoning. Death has followed a dose of 4 gm. of the solid acid, and recovery a dose of 30 gm. in solution. When death occurs, it may be almost instantaneously, usually within half an hour; sometimes after weeks or months, from secondary causes.

The treatment, which must be as expeditious as possible, consists in the administration, *first*, of lime or magnesia, or a soluble salt of Ca or Mg, suspended or dissolved in a *small* quantity of $H_2O$ or mucilaginous fluid; afterward, if vomiting have not occurred spontaneously, and if the symptoms of corrosion have not been severe, an emetic may be given. The alkaline carbonates are of no value in cases of oxalic-acid poisoning, as the oxalates which they form are soluble and almost as poisonous as the acid itself. The ingestion of water, or the administration of warm water as an emetic, is contraindicated when the poison has been taken in the solid form (or where doubt exists as to what form it was taken in), as they dissolve, and thus favor the absorption of the poison.

**Analysis.**—In fatal cases of poisoning by oxalic acid the contents of the stomach are sometimes strongly acid in reaction; more usually, owing to the administration of antidotes, neutral, or even alkaline. In a systematic analysis the poison is to be sought for in the residue of the portion examined for prussic acid and phosphorus; or, if the examination for those substances be omitted, in the ether-extract from the acid solution in the process for alkaloids. If oxalic acid alone is to be sought for, the contents of the stomach, or other substances *if acid*, are extracted with water, the liquid filtered, the filtrate evaporated, the residue extracted with alcohol, the alcoholic fluid evaporated, the residue redissolved in water (solution No. 1). The portion undissolved by alcohol is extracted with alcohol acidulated with hydrochloric acid, the solution evaporated after filtration, the residue dissolved in water (solution No. 2). Solution No. 1 contains any oxalic acid which may have existed free in the substances examined; No. 2 that which existed in the form of soluble oxalates. If lime or magnesia have been administered as an antidote, the substances must be boiled for an hour or two with potassium carbonate (not the hydroxid), filtered, and the filtrate treated as above. In the solutions so obtained oxalic acid is characterized by the tests given above.

The urine is also to be examined microscopically for crystals of calcium oxalate. The stomach may contain small quantities of oxalates as normal constituents of certain foods.

**Malonic Acid**—$CH_2\langle^{COOH}_{COOH}$—is a product of the oxidation of malic acid (p. 295), or of normal propyl glycol. It is best obtained by the general method 4, p. 285. Monochloracetic acid is converted into cyano-acetic acid by heating in alkaline solution with KCN: $CH_2Cl.COOH + KCN = CN.CH_2.COOH + KCl$. The cyano-acid is then hydrolysed by heating with KHO or HCl, thus: $CN.CH_2.COOH + 2H_2O = COOH.CH_2.COOH + NH_3$. It forms large prismatic crystals, soluble in water, alcohol and ether; fusible at 132° (269.6° F.), and decomposed at about 150° (302° F.) into acetic acid and carbon dioxid.

**Succinic Acid**—$\begin{matrix}CH_2—COOH\\ |\\ CH_2—COOH\end{matrix}$—118—exists in amber, coal, fossil wood, and in small quantity in animal and vegetable tissues. Its presence has been detected in the normal urine after the use of fruits and of asparagus, in the parenchymatous fluids of the spleen, thyroid, and thymus, and in the fluids of hydrocele and of hydatid cysts. It is also formed in small quantity during alcoholic fermentation; as a product of oxidation of many fats and fatty acids; and by synthesis from ethylene cyanid: $CN.(CH_2)_2.CN + 4H_2O = COOH.(CH_2)_2.COOH + 2NH_3$. It may also be obtained by dry distillation of amber, or by the fermentation of malic acid (p. 295).

It crystallizes in large prisms or hexagonal plates, which are colorless, odorless, permanent in air, acid in taste, soluble in water, sparingly so in ether and in cold alcohol. It fuses at 180° (356° F.), and distils with partial decomposition at 235° (455° F.). It withstands the action of oxidizing agents. Reducing agents convert it into the corresponding acid of the fatty series, butyric acid. With Br it forms products of substitution. $H_2SO_4$ is without action upon it. Phosphoric anhydrid removes $H_2O$ and converts it into **succinic anhydrid**, $C_4H_4O_3$.

**Isosuccinic Acid**—*Methyl-malonic acid*—$CH_3.CH\langle^{COOH}_{COOH}$—is formed by the action of hydrating agents upon α cyanopropionic acid. It forms prismatic crystals, fusible at 130° (266° F.), and is decomposed at higher temperatures into propionic acid and carbon dioxid.

**Glutaric Acid**—$COOH.(CH_2)_3.COOH$—*Normal Pyrotartaric acid*—the next superior homologue of succinic acid, is formed by reduction of α oxyglutaric acid (p. 295). It crystallizes in large plates, very soluble in water, which fuse at 27° (206.4 °F.). The corresponding amido-acid is one of the products of decomposition of protein bodies.

The **pyrotartaric acid** obtained by the action of heat on tartaric acid is **methyl-succinic acid**, $COOH.CH(CH_3).CH_2.COOH$, which may also be produced synthetically by the action of nascent H upon itaconic acid, $COOH.C(:CH_2).CH_2.COOH$, as well as by other methods. It fuses at 112° (233.6° F.), and forms rhombic prisms, very soluble in water, alcohol, and ether.

**Adipic Acid**—$COOH.(CH_2)_4.COOH$—is a product of the action of nitric acid on fats: **Pimelic acid**, $COOH.(CH_2)_5.COOH$, and **Suberic acid**, $COOH.(CH_2)_6.COOH$—are similarly obtained from cork. **Azelaic acid**, $C_9H_{16}O_4$, **Sebacic acid**, $C_{10}H_{18}O_4$, **Brassylic acid**, $C_{11}H_{20}O_4$, and **Rocellic acid**, $C_{17}H_{32}O_4$, also belong to this series.

### PARAFFIN TRI-, TETRA-, AND PENTA-CARBOXYLIC ACIDS.

**Tricarboxylic Acids** in which more than one carboxyl are attached to the same carbon atom exist only in their esters. The simplest of these: **Methenyl tricarboxylic ester**, $CH(COO.C_2H_5)_3$, is a crystalline solid, fusing at 29° (84.2° F.), and boiling at 253° (487.4° F.).

**Tricarballylic Acid**—$CH_2.(COOH).CH(COOH).CH_2(COOH)$—in which the carboxyls are attached to different carbon atoms, is a more stable compound. It exists in unripe beets and in the vacuum pan residues of beet-sugar works. It is formed by a variety of reactions, as by heating tribromhydrin with potassium cyanid and decomposing the cyanid with potash: $CH_2Br.CHBr.CH_2Br+3KCN=CH_2CN.CHCN.CH_2CN+3KBr$, and $CH_2CN.CHCN.CH_2CN+6H_2O=CH_2COOH.CH.COOH.CH_2COOH+3NH_3$. It forms rhombic prisms soluble in water, fusible at 164° (327.2° F.).

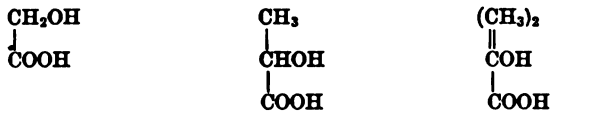
**Camphoronic Acid**—*aaβ* trimethyl-tricarballylic acid—$(CH_3)_2C(COOH).(CH_3)C(COOH).CH_2(COOH)$—is a product of oxidation of camphor (q. v.).

**Dimalonic Acid**—$\begin{matrix}COOH\\COOH\end{matrix}\!\!>\!CH.CH\!<\!\begin{matrix}COOH\\COOH\end{matrix}$—the simplest of the **tetracarboxylic acids**, is a crystalline solid, fusible at 168° (334.4° F.). On further heating it yields ethylene succinic acid: $(COOH)_2CH.CH(COOH)_2=COOH.CH_2.CH_2.COOH+2CO_2$.

**Propenyl-pentacarboxylic acid**—$C_3H_3(COOH)_5$—is also known.

### ALCOHOL-ACIDS—OXYACIDS.

These acids contain, besides the carboxyl group, one of the groups $CH_2OH$, CHOH, or COH, which characterize the primary, secondary, and tertiary alcohols. They, therefore, have the function of alcohols, primary, secondary, or tertiary, as well as that of acids:



Glycollic acid (primary). α Oxypropionic acid (secondary). α Oxyisobutyric acid (tertiary).

They may be considered as derived either from the di- and polyatomic alcohols (glycols, glycerols, etc.) by incomplete oxidation, as $COOH.CH_2OH$ from $CH_2OH.CH_2OH$; or from the pure acids by substitution of OH for H atoms in the remaining hydrocarbon groups, as $CH_2OH.CH_2.CH_2.COOH$; $CH_2OH.CHOH.CH_2.COOH$, and $CH_2OH.CHOH.CHOH.COOH$ from $CH_3.CH_2.CH_2.COOH$.

The *basicity* of these acids is represented by the number of carboxyl groups which they contain, their *atomicity* by the number of hydroxyls. Thus $CH_2OH.CHOH.COOH$ is monobasic and triatomic.

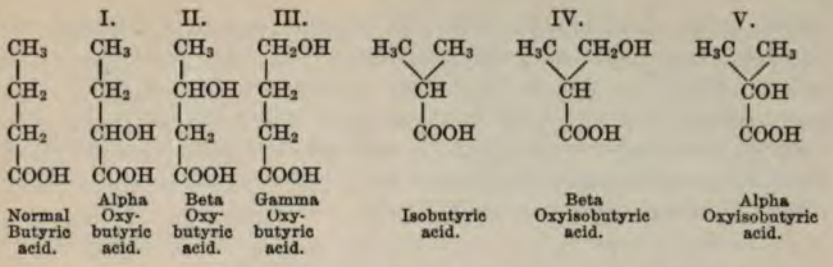
The algebraic formulæ of the several monobasic series are $C_nH_{2n}O_3$; $C_nH_{2n}O_4$, $C_nH_{2n}O_5$, etc., those of the dibasic series $C_nH_{2n-2}O_5$, $C_nH_{2n-2}O_6$, etc.; and those of the tribasic series $C_nH_{2n-4}O_7$, $C_nH_{2n-4}O_8$, etc.

### OXYACETIC SERIES. $C_nH_{2n}O_3$.

The acids of this series contain one carboxyl and one alcoholic group. They are, therefore, monobasic and diatomic, and may be considered as derived from the glycols by oxidation of one $CH_2OH$ group, or from the acids of the acetic series by substitution of OH for H in a hydrocarbon group (oxyacetic).

They are formed: (1) By the limited oxidation of the corresponding glycols or oxyaldehydes: $CH_2OH.CH_2OH+O_2=CH_2OH.COOH+H_2O$, or, $2CH_2OH.CHO+O_2=2CH_2OH.COOH$; (2) By the action of nascent hydrogen upon the aldehyde or ketone acids (p. 297), or upon the acids of the oxalic series: $CHO.COOH+H_2=CH_2OH.COOH$, or, $CH_3.CO.COOH+H_2=CH_3.CHOH.COOH$, or, $COOH.COOH+2H_2=CH_2OH.COOH+H_2O$; (3) By heating the monohalogen fatty acids with silver or potassium hydroxids, or with water: $CH_2Cl.COOH+KHO=CH_2OH.COOH+KCl$, or, $CH_2Cl.COOH+H_2O=HCl+CH_2OH.COOH$; (4) From the aldehydes and ketones, by their conversion, first into oxycyanids by the action of hydrocyanic acid: $CH_3.CHO+HCN=CH_3.CH\langle^{OH}_{CN}$, and the action upon these of acids or alkalies: $CH_3.CH\langle^{OH}_{CN}+2H_2O=CH_3.CHOH.COOH+NH_3$.

**Isomeres—Position or Place Isomery.**—Considering the oxybutyric acids as derived from normal and isobutyric acids by substitution of one OH for a hydrogen atom in a hydrocarbon group, the following five derivatives are possible:




While III, IV, and V are obviously different in molecular structure from each other and from I and II, in that the latter contain the group CHOH, while the former contain the groups $CH_2OH$,CH, and COH, the only difference between I and II, whose molecules are composed of identical groups, is in the *position* or *place* of the alcoholic hydroxyl with reference to the carboxyl group. **Place isomeres** of this kind are distinguished by designating that in which the second substituted group (in this case the OH) is attached to the carbon atom contiguous to the first as the alpha, or 1-compound, and the others by the succeeding Greek letters, or by the numerals in the order of the removal of the position of the second substitution. Thus II above is Beta oxybutyric or 2-oxybutyric acid. (See Orientation, p. 381.)

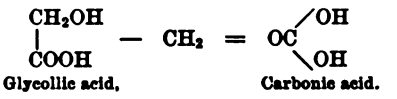
The $\alpha$, $\beta$, $\gamma$, and $\delta$ acids differ in their products of dehydration: The $\alpha$ acids yields cyclic double esters, called **lactids**, by elimination of $H_2O$ from two molecules of the acid (p 320). The $\beta$ acids are converted into unsaturated acids by loss of $H_2O$ from one molecule of the acid: $CH_2OH.CH_2.COOH = CH_2{:}CH.COOH + H_2O$. The $\gamma$ and $\delta$ acids, and those of greater carbon content, are converted into simple cyclic esters, called **lactones**, by elimination of $H_2O$ from a single molecule of the acid (p. 320).

By further oxidation the primary oxyacids containing $CH_2OH$ yield aldehyde acids: $2CH_2OH.COOH + O_2 = 2CHO.COOH + 2H_2O$, and then dibasic acids: $2CHO.COOH + O_2 = 2COOH.COOH$; the secondary acids, containing CHOH, yield ketone acids: $2CH_3.CHOH.COOH + O_2 = 2CH_3.CO.COOH + 2H_2O$, and the tertiary acids, containing COH, yield ketones, carbon dioxid and water: $2\,(CH_3)_2COH.COOH + O_2 = 2CH_3.CO.CH_3 + 2CO_2 + 2H_2O$.

The hydrogen of their carboxyl group may be replaced to form salts, esters, or amids; and the hydroxyl of their alcoholic group may be replaced by alkali metals, alkyls, or acidyls. In other words, they behave as acids and as alcohols.

**Oxyformic Acid—Carbonic acid**— $OC(OH)_2$.—Although this acid does not exist free, but is decomposed as soon as liberated into $CO_2$ and $H_2O$ (p. 225), its salts, the carbonates, are well known and quite

stable. The position of this acid in this series is an apparent anomaly, as it is dibasic, not monobasic like the other terms of the series. But if we bear in mind that the basic nature of the H atom in a hydroxyl depends upon its close union with a CO group (or some other electro negative group), it is evident that the two H atoms in the inferior homologue of glycollic acid, being similarly united to the same CO group, must be equally basic:




Glycollic acid. Carbonic acid.

Indeed, carbonic acid is not an alcohol acid, but a pure acid, as it contains no alcoholic group.

Esters are also known corresponding to orthocarbonic acid: $C(OH)_4$, although the acid itself is unknown.

**Glycollic Acid—Oxyacetic acid**—$CH_2OH.COOH$—is formed by the oxidation of glycol, by the action of nitrous acid upon glycocoll, and by the action of KHO upon monochloracetic acid, or upon glyoxal, CHO.CHO.

It forms deliquescent acicular crystals, very soluble in water, alcohol and ether. It fuses at 80° (176° F.). It is oxidized by $HNO_3$ to oxalic acid.

**Lactic Acids—Oxypropionic acids**—*Alpha oxypropionic acid—Ethidene lactic acid*—$CH_3.CHOH.COOH$—is formed from milk sugar, cane sugar, gum and starch by *lactic fermentation*, induced by the lactic acid bacillus. It consequently exists in many soured products, such as soured milk, sour-krout, fermented beet-juice, and the waste liquors of starch works and of tanneries. It is formed in the stomach during digestion of carbohydrates. It is prepared by allowing a mixture of cane sugar, tartaric acid, rotten cheese, skim milk and chalk to ferment for ten days at 35° (95° F.). It has also been obtained by oxidation of alpha propylene glycol: $CH_3.CHOH.CH_2OH+O_2=CH_3.CHOH.COOH+H_2O$.

Lactic acid of fermentation is a colorless, or yellowish, syrupy liquid; sp. gr. 1.215 at 20° (68° F.); soluble in water, alcohol and ether. It does not distil without decomposition, but when heated it yields lactid (p. 320), carbon monoxid, aldehyde and water. Oxidizing agents convert it into pyroracemic acid: $CH_3.CO.COOH$; or, if more energetic, split it up into acetic acid and carbon dioxid: $CH_3.CHOH.COOH+O_2=CH_3.COOH+CO_2+H_2O$. Heated to 130° (266° F.) with dilute sulfuric acid it splits into aldehyde and formic acid: $CH_3.CHOH.COOH=CH_3.CHO+H.COOH$. Hydriodic acid reduces it to propionic acid; but hydrobromic acid converts it into α-bromopropionic acid.

Ethidene lactic acid contains an asymmetric carbon atom (p. 267): $CH_3.*CHOH.COOH$; and that produced by lactic fermentation is optically inactive (d+l). The **dextro** acid, also known as **sarcolactic** or **paralactic acid**, is best obtained from Liebig's meat extract; and is also produced by allowing *Penicillium glaucum* to grow in a solution of inactive ammonium lactate. It exists in muscular tissue after death and during contraction, and in the spleen, lymphatic glands, thymus, thyroid, blood, bile, transudates, in the perspiration in puerperal fever, and in the urine after violent exercise, in yellow atrophy of the liver and in phosphorus poisoning, either free or in combination. The acid in muscular tissue probably originates from glycogen.

**Laevolactic Acid** is formed by the growth of *Bacillus acidi laevolactici* in a solution of cane sugar.

**Ethylene Lactic Acid — Beta oxypropionic acid — Hydracrylic acid**—$CH_2OH.CH_2.COOH$—the third form of lactic acid, is formed by the action of moist silver oxid upon $\beta$-iodo- or $\beta$-chloropropionic acid; by the saponification of ethylene cyanhydrin; or by the oxidation of the corresponding glycol. It is a thick, uncrystallizable syrup, which is converted by dehydration into acrylic acid $CH_2OH.CH_2.COOH = CH_2:CH.COOH + H_2O$. On oxidation it yields oxalic acid and carbon dioxid: $2(CH_2OH.CH_2.COOH) + 5O_2 = 2(COOH.COOH) + 2CO_2 + 4H_2O$.

**Oxybutyric Acids.**—Five isomeres are possible (p. 291). **Beta oxybutyric acid**—$CH_3.*CHOH.CH_2.COOH$, is formed by the action of sodium amalgam upon acetoacetic ester (p. 313) $CH_3.CO.CH_2.COOH + H_2 = CH_3.CHOH.CH_2.COOH$. The lævo-acid, a colorless syrup, readily soluble in water, alcohol and ether, occurs, accompanied by acetoacetic acid, in the blood and urine in severe cases of diabetes.

**Alpha Oxycaproic Acid**—$CH_3.(CH_2)_3.CHOH.COOH$—is **leucic acid**, obtained by oxidizing leucin (p. 365) by nitrous acid.

### HIGHER MONOCARBOXYLIC OXYACIDS.

Representatives of the following series are known:

**Dioxymonocarboxylic Series, Glyceric Series**—$C_nH_{2n}O_4$.—The acids of this series bear the same relation to the glycerols that those of the oxyacetic series bear to the glycols. **Glyceric acid**, $CH_2OH.*CHOH.COOH$, is an uncrystallizable syrup obtained by the limited oxidation of glycerol.

**Trioxymonocarboxylic Series**—$C_nH_{2n}O_5$—of which **erythritic, or erythroglucic acid**: $CH_2OH.(CHOH)_2.COOH$, derived from erythrol (p. 254) is the first term.

**Tetroxymonocarboxylic Series**—$C_nH_{2n}O_6$—are obtained by oxidation of the aldopentoses (p. 264).

**Pentoxymonocarboxylic Series**—$C_nH_{2n}O_7$—are obtained by oxidation of the hexahydric alcohols and aldohexoses. Synthetically, they are produced from the aldopentoses, by their conversion into nitrils of the oxyacids by CNH, and the action upon these of HCl, thus l-arabinose $CH_2OH.(CHOH)_3.CHO$ yields l-gluconononitril, $CH_2OH.(CHOH)_3.CH(OH)CN$, and this yields l-gluconic acid, $CH_2OH.(CHOH)_4.COOH$.

These acids are very unstable when free, easily losing water to form lactones (p. 320). They readily unite with phenylhydrazin to form phenylhydrazids, such as gluconophenyl hydrazid: $CH_2OH.(CHOH)_4.CO.NH.NH.C_6H_5$, which crystallize in characteristic forms (pp. 264, 430). They form numerous space isomeres. Their lactones treated with sodium amalgam, take up $H_2$ and produce the corresponding aldohexoses: thus gluconolactone yields glucose.

**Mannonic Acids**—$C_5H_6(OH)_5.COOH$.—The three acids, d-, l-, and (d+l), derived from the corresponding mannitols, yield the corresponding dibasic mannosaccharic acids on oxidation. They are syrupy liquids, which are converted into their lactones by evaporation of their solutions. On heating d- and l-mannonic acids with quinolin to 140° (284° F.), they are, in part, converted into d- and l-gluconic acids. By this action and the subsequent conversion of gluconolactone, referred to above, glucose may be synthetically obtained from mannitol.

**Gluconic Acids**—$CH_2OH.(CHOH)_4.COOH$.—The d-, l-, and (d+l) acids are known. By oxidation they yield the corresponding saccharic acids. The lactones yield d-, l-, and (d+l) glucose by reduction. *d-Gluconic acid*, also known as **dextronic** or **maltonic acid**, is a syrup which forms a crystalline lactone on evaporation of its solution. It is formed by oxidizing dextrose, dextrin, starch, cane sugar, or maltose by chlorin or bromin water.

Acids belonging to the still higher series $C_nH_{2n}O_8$, $C_nH_{2n}O_9$, and $C_nH_{2n}O_{10}$, corresponding to the heptoses, octoses and nonoses (p. 264) are also known.

### MONOXYDICARBOXYLIC SERIES—$C_nH_{2n-2}O_5$.

The acids of this series contain two carboxyls and one alcoholic group. They are, therefore, dibasic and triatomic, and may be considered as derived from the glycerols by oxidation of both $CH_2OH$ groups. They may also be considered as derived from the paraffin dicarboxylic acids (oxalic series), above the first, by substitution of OH for H in a hydrocarbon group, in the same manner as the acids

of the oxyacetic series are derived from those of the acetic series (p. 290).

**Tartronic Acid — Oxymalonic acid** — COOH.CHOH.COOH — is formed by the action of moist silver oxid upon monochloro- or monobromo-malonic acid, or by oxidation of glycerol by potassium permanganate. It crystallizes in large prisms, readily soluble in water, alcohol, and ether, and fusible at 184° (363.2° F.).

**Malic Acid — Oxysuccinic acid** — $COOH.CH_2.*CHOH.COOH$ — exists in three modifications. The lævo-acid exists free, and in combination with K, Na, Ca, Mg, and organic bases in apples, pears, and similar fruits, and in the berries of the mountain ash and in gooseberries. The inactive (d+l), acid may be obtained from monobromo-succinic acid by the action either of moist silver oxid, of dilute HCl, of dilute NaHO, or even of boiling water; and by several other methods. The dextro-acid is obtained by the reduction of dextrotartaric acid by hydriodic acid.

The natural malic acid crystallizes in prismatic needles; odorless; acid in taste; fusible at 100° (212° F.); deliquescent; very soluble in water and in alcohol. Heated to 140° (284° F.) it loses water with formation of fumaric acid, COOH.CH:CH.COOH. At 180° (356° F.) it yields water, fumaric acid and maleïc anhydrid, $\begin{matrix} CH.CO \\ \| \quad \quad O \\ CH.CO \end{matrix}$. Reducing agents convert it into succinic acid. The malates are oxidized to carbonates in the body.

**Oxyglutaric Acid** exists in the two isomeres: α oxyglutaric acid, $COOH.CH(OH).CH_2.CH_2.COOH$, which occurs in molasses, crystallizes with difficulty, and fuses at 72° (161.6° F.); and β oxyglutaric acid, $COOH.CH_2.CHOH.CH_2.COOH$, which fuses at 95° (203° F.).

### DIOXYDICARBOXYLIC ACIDS — $C_nH_{2n-2}O_6$.

**Tartaric Acids — Dioxyethylene Succinic Acids.** — There exist four acids having the composition $C_4H_6O_6$, which are readily convertible one into the other. They are: *Dextro-tartaric*, or *ordinary tartaric acid; lævo-tartaric acid*; *mesotartaric*, or *antitartaric acid*; and *racemic*, or *paratartaric acid*. The first three of these are stereoisomeres, due to the presence of two asymmetric carbon atoms in the molecule, whose molecular structure has been discussed under the head of space isomery (p. 267). Mesotartaric acid, which is optically inactive, has a molecular structure differing from those of the d- and l- acids, into which it cannot be split. Racemic acid, also optically inactive, is the (d+l) acid, and can be readily decomposed into them or separated from a mixture of them.

*Dextro-tartaric Acid—Ordinary tartaric acid—Acidum tartaricum*

(U. S.; Br.)—occurs, both free and in combination, in the sap of the vine and in many other vegetable juices and fruits, particularly in grape-juice. Although this is probably the only tartaric acid existing in nature, all four varieties may occur in the commercial acid, being formed during the process of manufacture. Tartaric acid is obtained in the arts from hydropotassic tartrate, or cream of tartar (p. 179).

The ordinary tartaric acid crystallizes in large prisms; very soluble in $H_2O$ and in alcohol; acid in taste and reaction. Heated with water at 165°–175° (329°–347° F.) it is converted into mesotartaric and racemic acids. It fuses at 170° (338° F.); at 180° (356° F.) it loses $H_2O$, and is gradually converted into an anhydrid; at 200°–210° (392°–410° F.) it is decomposed with formation of pyruvic acid, $C_3H_4O_3$ (p. 298), and pyrotartaric acid, $C_5H_8O_4$, (p. 289); at higher temperatures $CO_2$, CO, $H_2O$, hydrocarbons and charcoal are produced.

Tartaric acid is attacked by oxidizing agents with formation of $CO_2$, $H_2O$, and, in some instances, formic and oxalic acids. Certain reducing agents convert it into malic and succinic acids. With fuming $HNO_3$ it forms a dinitro-compound, which is very unstable, and which, when decomposed below 36° (96.8° F.), yields tartaric acid. It forms a precipitate with lime-water, soluble in an excess of $H_2O$. In not too dilute solution it forms a precipitate with potassium sulfate solution. It does not precipitate with the salts of Ca. When heated with a solution of auric chlorid it precipitates the gold in the metallic form.

When taken into the economy, as it frequently is in the form of tartrates, the greater part is oxidized to carbonic acid (carbonates); but, if taken in sufficient quantity, a portion is excreted unchanged in the urine and perspiration. The free acid is poisonous in large doses. The acids and its salts are largely used in pharmacy and in dyeing.

*Lævo-tartaric*—forms crystals similar to those of the dextro acid, but having opposite hemihedral facets (p. 11), so that the crystals of one acid resemble the reflection of those of the other in a mirror.

*Racemic Acid—(d+l) Tartaric acid*—is produced when concentrated solutions of equal quantities of d- and l-tartaric acids are mixed. It is formed by oxidation of dulcitol and of mannitol. It is obtained by the action of moist silver oxid upon dibromo succinic acid: $COOH.CHBr.CHBr.COOH + 2AgHO = COOH.CHOH.CHOH.COOH + 2AgBr$; and by several other synthetic methods. It crystallizes in rhombic prisms, less soluble in water than ordinary tartaric acid, and fuses at 205° (410° F.).

*Mesotartaric Acid—Inactive Tartaric acid*—is obtained by oxidation of erythrol; or by heating dextrotartaric acid with water at 165° (329° F.) for two days.

### HIGHER DICARBOXYLIC OXYACIDS.

The carbohydrates, on oxidation with nitric acid, yield *tetroxydicarboxylic acids:* $COOH.(CHOH)_4.COOH$. Among these are: **mannosaccharic acids**, derived from the mannonic acids (p. 294); **saccharic acids**; and **mucic acid.** Of the three saccharic acids the d-acid is the best known. It is produced by oxidation of many carbohydrates, including cane sugar and grape sugar, by nitric acid, and by the action of bromin water on glucuronic acid (p. 299). Nascent H reduces it to glucuronic acid. It forms a syrup or a deliquescent solid, which, on standing, changes to a crystalline lactone. Mucic acid is produced by the oxidation of dulcitol, milk sugar, and the gums. It is a white solid, almost insoluble in cold water and in alcohol, which fuses at 210° (410° F.). When heated it loses $CO_2$ and forms *pyromucic*, or *furfurane monocarboxylic acid* (p. 455).

**Pentoxydicarboxylic acids** are also known, of which the type is *pentoxypimelic acid:* $COOH.(CHOH)_5.COOH$.

### OXYTRICARBOXYLIC ACIDS—$C_nH_{2n-4}O_7$.

**Citric Acid**—$HO.C(CH_2.COOH)(COOH)(CH_2.COOH)$, exists in the juices of many fruits, lemon, strawberry, currant, and in small quantity, as calcium citrate, in cow's milk. It is obtained commercially from lemon juice. It crystallizes in large, rhombic prisms, very soluble in water and in alcohol. It fuses at 100° (212° F.); at 175° (347° F.) it is decomposed with loss of water and formation of **aconitic acid** (p. 376); and at a higher temperature $CO_2$ is given off and **citraconic** and **itaconic acids** are produced. In the body its salts are oxidized to carbonates.

### ALDEHYDE-ACIDS.

These are substances having both aldehyde and acid functions, and containing the groups CHO and COOH. The simplest of the class is formic acid, already referred to as the first term of the acetic series (p. 278), in which, however, the carbon atom is common to the two groups: $O:C(H)(OH)$.

**Glyoxylic Acid**—$CHO.COOH$—when produced unites with water to form a hydrate: $(OH)_2:CH.COOH$, corresponding to chloral hydrate (p. 259) : $(OH)_2:CH.CCl_3$. This is a thick syrup, or it forms rhombic prisms. It is produced by heating dichloracetic acid with water at 230° (446° F.) : $CHCl_2.COOH+H_2O=CHO.COOH+2HCl$. It has the reducing power and other properties of the aldehydes.

### KETONE-ACIDS.

These compounds contain both the ketonic and carboxyl groups, CO and COOH.

The **monoketone-monocarboxylic acids** contain one CO and one COOH. According as the CO group occupies the position adjacent to the carboxyl, or further removed therefrom, these acids are designated as $\alpha$, $\beta$, $\gamma$, etc.; thus $CH_3.CH_2.CO.COOH=\alpha$, $CH_3.CO.CH_2.COOH=\beta$, etc.

The $\alpha$, $\gamma$, $\delta$, etc., acids are much more stable than the $\beta$-acids, and may be obtained by oxidation of the corresponding secondary alcohol acids. The $\alpha$ acids are derivable from formic acid by substitution of acidyls for the extra-carboxylic hydrogen: $(CH_3.CO).COOH$.

**Pyruvic Acid**—*Pyroracemic acid*—$CH_3.CO.COOH$—is formed by oxidation of $\alpha$-oxypropionic acid: $2CH_3.CHOH.COOH+O_2=2CH_3.CO.COOH+2H_2O$. It is also formed by distillation of tartaric acid: $COOH.CHOH.CHOH.COOH=CH_3.CO.COOH+CO_2+H_2O$.

The $\beta$-ketone acids are more unstable, and are decomposed by heat with formation of ketone and carbon dioxid: $COOH.CH_2.CO.CH_3=CO_2+CH_3.CO.CH_3$. Their esters are, however, quite stable, and are employed in many syntheses. The $\beta$ acids bear the same relation to acetic acid that the $\alpha$ acids do to formic acid: $(CH_3.CO).CH_2.COOH$.

**Aceto-acetic Acid**—$CH_3.CO.CH_2.COOH$—may be obtained as a thick, strongly acid liquid by saponification of its esters. Heat decomposes it into acetone and carbon dioxid, according to the equation given above. Aceto-acetic acid accompanies $\beta$-oxybutyric acid and acetone in the urine in diabetes. (See Aceto-acetic ester, p. 313). **Diketone-monocarboxylic acids**, such as $CH_3.CO.CO.COOH$, are also known, as well as **triketone monocarboxylic acids**, and **mono-, di-, and triketone dicarboxylic acids. Aldehyde-ketone acids**, such as CHO.CO.COOH, also exist.

**Mesoxalic Acid—Dioxymalonic acid**—$\begin{matrix}HO\\HO\end{matrix}\!\!>\!C\!<\!\!\begin{matrix}COOH\\COOH\end{matrix}$—is the monoketone-dicarboxylic acid, COOH.CO.COOH, combined with water in the same manner as chloral hydrate and glyoxylic acid (see above and pp. 225, 259). Esters are known corresponding to both forms: **oxymalonic esters**, $CO:(COO.C_2H_5)_2$, and **dioxymalonic esters**, $C(OH)_2:(COO.C_2H_5)_2$. Mesoxalic acid is obtained by the action of boiling barium hydroxid upon dibromomalonic acid: $COOH.CBr_2.COOH+Ba(OH)_2=COOH.C(OH)_2.COOH+BaBr_2$, or upon alloxan (mesoxalylurea). It crystallizes in prisms, very soluble in water, fusible at 115° (239° F.) On evaporation of its aqueous solution it decomposes into carbon monoxid, water and oxalic acid; at higher temperatures it yields carbon dioxid and glyoxylic acid.

## OXYALDEHYDE AND OXYKETONE ACIDS.

These acids contain alcoholic groups, $CH_2OH$, CHOH, or COH in addition to carboxyl and either the aldehyde or ketone group, CHO or CO.

**Glucuronic Acid**—$CHO.(CHOH)_4.COOH$—is a derivative of glucose: $CHO.(CHOH)_4.CH_2OH$. It is a syrup which passes into a crystalline lactone on warming. It occurs in the urine in small quantity normally, in combination with phenol, skatole and indole, and with camphors, chloral and other substances when these are present.

## SIMPLE ETHERS.

These substances have been referred to (p. 237) as the simplest products of oxidation of the hydrocarbons. The term *ether* was formerly applied to any substance produced by the action of an acid upon an alcohol. Such products belong, however, to two distinct classes:

(1) **The simple ethers, or ethers,** which are the oxids of the hydrocarbon radicals, and the counterparts of the metallic oxids, bearing the same relation to the alcohols that the metallic oxids do to their hydroxids:

| $(CH_3.CH_2)_2O$ | $(CH_3.CH_2)(H)O$ | $K_2O$ | $(K)(H)O$ |
|---|---|---|---|
| Ethyl oxid. (Ether.) | Ethyl hydroxid. (Alcohol). | Potassium oxid. | Potassium hydroxid. |

(2) **The compound ethers,** now called **esters,** which are the products of the reaction between an acid and the alcohol, the latter behaving as a basic hydroxid (p. 239). They are the counterparts of the metallic salts:

| $(CH_3.CH_2.O)(HO)SO_2$ | $(CH_3.CH_2.O)_2SO_2$ | $(KO)(HO)SO_2$ | $(KO)_2SO_2$ |
|---|---|---|---|
| Monoethylic sulfate. (Ester-acid.) | Diethylic sulfate. (Neutral ester.) | Monopotassic sulfate. (Acid salt.) | Dipotassic sulfate. (Neutral salt.) |

**Mixed ethers** differ from simple ethers in that they contain different, in place of similar, alkyls, as **methyl-ethyl oxid:** $CH_3.O.CH_2.CH_3$

Simple and mixed ethers are formed: (1) By interaction of the alcohols and alkyl-sulfuric acids. Thus methyl-sulfuric acid and ethylic alcohol form methyl-ethyl oxid: $SO_2\langle^{O.CH_3}_{OH} + C_2H_5.O.H = C_2H_5.O.CH_3 + SO_2:(OH)_2$. (2) By the action of alkyl haloids upon sodium alcoholates: $CH_3.Cl + C_2H_5.O.Na = NaCl + C_2H_5.O.CH_3$. (3) By the action of silver oxid upon alkyl haloids: $2C_2H_5I + Ag_2O = 2AgI + O\ (C_2H_5)_2$.

**Methyl oxid**—$CH_3.O.CH_3$—46—isomeric with ethyl alcohol, is obtained by the action of silver oxid upon methyl iodid, or by the action of $H_2SO_4$ and boric acid upon methyl alcohol. It is a colorless gas, has an ethereal odor, burns with a pale flame, liquefies at —36° (—32.8° F.), and boils at —21° (—5.8° F.), is soluble in $H_2O$, $H_2SO_4$ and ethylic alcohol.

**Ethyl Oxid**—*Ethylic ether*—*Sulfuric ether*—*Æther fortier* (U. S.); *Æther purus* (Br.)—$C_2H_5.O.C_2H_5$.—In the manufacture of ether a mixture is made of 5 pts. of 90% alcohol and 9 pts. of concentrated $H_2SO_4$, in a vessel surrounded by cold water, This mixture is introduced into a retort, into which a slow stream of alcohol is allowed to flow during the remainder of the process. Heat, so regulated as not to exceed 140° (284° F.), is then applied to the retort, which is connected with a well-cooled condenser, and continued until the temperature rises above the point indicated. The distillate contains ether, alcohol, water and dissolved gases, notably $SO_2$. It is shaken with water containing potash or lime, and the ether decanted off. The product is "washed ether." For further purification it is treated with calcium chlorid, or recently burnt lime, with which it is left in contact for 24 hours, and from which it is then distilled.

In the conversion of alcohol into ether, sulfovinic or ethyl-sulfuric acid behaves as a "contact substance" and serves to carry an ethyl radical from one alcohol molecule to another, with formation of water and regeneration of sulfuric acid. In the first stage of the reaction ethyl-sulfuric acid is formed by the action of $H_2SO_4$ upon alcohol, molecule for molecule: $H_2SO_4+C_2H_5.OH=H_2O+C_2H_5.HSO_4$. The ethyl-sulfuric acid then reacts with another molecule of alcohol, according to the general reaction (1) for the formation of ethers, to form ether and sulfuric acid: $C_2H_5.HSO_4 + C_2H_5.OH = H_2SO_4 + (C_2H_5)_2O$. It would seem, therefore, that a given quantity of $H_2SO_4$ could convert an unlimited amount of alcohol into ether. But the gradual accumulation of the $H_2O$ formed in the first stage of the reaction, and the occurrence of secondary reactions in practice limit the amount of ether produced to about four or five times the bulk of acid used.

Ether is a colorless liquid; has a sharp, burning taste, and a peculiar, tenacious odor, characterized as ethereal. Sp. gr. 0.723 at 12.5° (54.5° F); it boils at 34.5° (94.1° F.). Its tension of vapor is very great, especially at high temperatures; and it is exceedingly volatile. Water dissolves one-ninth its weight of ether. Ethylic and methylic alcohols are miscible with it in all proportions. Ether is an excellent solvent of many substances not soluble in water and alcohol. The resins and fats are readily soluble in ether. The salts of the alkaloids and many vegetable coloring matters are soluble in

alcohol and water, but insoluble in ether, while the free alkaloids are for the most part soluble in ether, but insoluble, or very sparingly soluble, in water.

Ether is highly inflammable; and burns with a luminous flame. The vapor forms with air a violently explosive mixture. It is denser than air, through which it falls and diffuses itself to a great distance; caution is therefore required in handling ether in a locality in which there is a light or fire, especially if the fire be near the floor.

Pure ether is neutral in reaction. $H_2SO_4$ mixes with it, with elevation of temperature, and formation of sulfovinic acid. With sulfuric anhydrid it forms ethyl sulfate. $HNO_2$, aided by heat, oxidizes it to carbon dioxid and acetic and oxalic acids. Ether, saturated with HCl and distilled, yields ethyl chlorid. Cl, in the presence of $H_2O$, oxidizes it, with formation of aldehyde, acetic acid, and chloral. In the absence of $H_2O$, however, a series of products of substitution are produced, in which 2, 4, and 10 atoms of H are replaced by a corresponding number of atoms of Cl. These substances in turn, by substitution of alcoholic radicals, or of atoms of elements, for atoms of Cl, give rise to other derivatives.

**Action on the Economy.**—Ether is largely used in medicine for producing anæsthesia, either locally by diminution of temperature, due to its rapid evaporation, or generally by inhalation. When taken in overdoses, it causes death, although it is by no means as liable to give rise to fatal accidents as is chloroform. Patients suffering from an overdose may, in the vast majority of cases, be resuscitated by artificial respiration and the induced current, one pole to be applied to the nape of the neck, and the other carried across the body just below the anterior attachments of the diaphragm.

In cases of death from ether the odor is generally well marked in the clothing and surroundings, and especially on opening the thoracic cavity. In the analysis it is sought for in the blood and lungs at the same time as chloroform (p. 235).

**Ethylene Oxid**—$\begin{matrix}CH_2\diagdown\\ |\quad O\\ CH_2\diagup\end{matrix}$—is a cyclic ether corresponding to glycol: $CH_2OH.CH_2OH=(CH_2)_2O+H_2O$, as ethyl oxid corresponds to ethylic alcohol: $2CH_3,CH_2.OH=(C_2H_5)_2O+H_2O$. It is prepared by the action of caustic potash on ethylene chlorhydrin (p. 315): $CH_2OH.CH_2Cl+KHO=(CH_2)_2O+KCl+H_2O$. It is a volatile liquid, boils at 13.5° (54.3° F.), is neutral in reaction and mixes with water. It unites with $H_2O$ to form glycol, and with HCl to regenerate ethylene chlorhydrin. Nascent H converts it into ethyl alcohol. Aliphatic ethers are also derivable from the glycols, such as **glycol diethyl ether**, $C_2H_5.O.C_2H_4.O.C_2H_5$, and **diethylene glycol ether**, $HOCH_2.CH_2.O.CH_2.CH_2OH$.

### ANHYDRIDS.

The organic anhydrids are the oxids of the acid radicals (acidyls); and bear the same relation to the acids that the simple ethers bear to the alcohols:

| | |
|---|---|
| $CH_3.COOH$ | $CH_3.CH_2OH$ |
| Acetic acid. | Ethylic alcohol. |
| $CH_3.CO\rangle O$ <br> $CH_3.CO\rangle$ | $CH_3.CH_2\rangle O$ <br> $CH_3.CH_2\rangle$ |
| Acetic anhydrid. | Ethylic ether. |

The two oxids of carbon are also anhydrids in that they combine with water to produce acids, or, what amounts to the same thing, with KHO to form the K salts, thus:

| | | | | |
|---|---|---|---|---|
| CO | + | KHO | = | H.COOK |
| Carbon monoxid. | | Potassium hydroxid. | | Potassium formate. |
| $CO_2$ | + | KHO | = | $O{:}C\langle^{OH}_{OK}$ |
| Carbon dioxid. | | Potassium hydroxid. | | Monopotassic carbonate. |

### OXIDS OF CARBON.

**Carbon Monoxid—Carbonous oxid—Carbonic oxid**—CO—28—is formed: (1) By burning C with a limited supply of air. (2) By passing dry carbon dioxid over red-hot charcoal. (3) By heating oxalic acid with sulfuric acid $C_2O_4H_2 = H_2O + CO + CO_2$; and passing the gas through sodium hydroxid to separate $CO_2$. (4) By heating potassium ferrocyanid with $H_2SO_4$.

It is a colorless, tasteless gas: sp. gr. 0.9678A; very sparingly soluble in $H_2O$ and in alcohol. It burns in air with a blue flame to $CO_2$, and it forms explosive mixtures with air and oxygen. It is a valuable reducing agent, and is used for the reduction of metallic oxids at a red heat. Ammoniacal solutions of the cuprous salts absorb it readily. Being non-saturated, it unites readily with O to form $CO_2$, and with Cl to form $COCl_2$, the latter a colorless, suffocating gas, known as **phosgene**, or **carbonyl chlorid**, which is of service in the formation of acid chlorids and anhydrids (p. 310) and in a variety of other syntheses.

**Toxicology.**—Carbon monoxid is an exceedingly poisonous gas, and is the chief toxic constituent of the gases given off from blast-furnaces, from defective flues, from open coal or charcoal fires; and of illuminating gas.

Poisoning by CO may occur in several ways. By inhalation of the gases discharged from blast-furnaces and from copper-furnaces, the former containing 25 to 32 per cent. and the latter 13 to 19 per

cent. of CO. By the fumes given off from charcoal burned in a confined space, which consists of a mixture of the two oxids of carbon, the dioxid predominating largely, especially when the combustion is most active. The following is the composition of an atmosphere produced by burning charcoal in a confined space, and which proved rapidly fatal to a dog: oxygen, 19.19; nitrogen, 76.62; carbon dioxid, 4.61; carbon monoxid, 0.54; marsh-gas, 0.04. Obviously the deleterious effects of charcoal-fumes are more rapidly fatal in proportion as the combustion is imperfect and the room small and ill-ventilated.

A fruitful source of CO poisoning, sometimes fatal, but more frequently producing languor, headache and debility, is to be found in the stoves, furnaces, etc., used in heating our dwellings and other buildings, especially when the fuel is anthracite coal. This fuel produces in its combustion, when the air supply is not abundant, considerable quantities of CO, to which a further addition may be made by the reduction of the dioxid, also formed, in passing over red-hot iron.

Of late years cases of fatal poisoning by illuminating gas are of very frequent occurrence, caused either by accidental inhalation, by inexperienced persons blowing out the gas, or by suicides. The most actively poisonous ingredient of illuminating gas is CO, which exists in the ordinary coal-gas in the proportion of 4 to 7.5 per cent., and in water-gas, made by decomposing superheated steam by passage over red-hot coke, and subsequent charging with vapor of hydrocarbons, in the large proportion of 30–35 per cent.

The method in which CO produces its fatal effects is by forming with the blood-coloring matter a compound which is more stable than oxyhæmoglobin, and thus causing asphyxia by destroying the power of the blood corpuscles of carrying O from the air to the tissues. This compound of CO and hæmoglobin is quite stable, and hence the symptoms of this form of poisoning are very persistent, lasting until the place of the coloring-matter thus rendered useless is supplied by new formation. The prognosis is very unfavorable when the amount of the gas inhaled has been at all considerable, the treatment usually followed, *i.e.*, artificial respiration and inhalation of O, failing to restore the altered coloring matter. There would seem to be no form of poisoning in which transfusion of blood is more directly indicated than in that by CO, but it has been found to be detrimental rather than beneficial.

**Detection after death.**—The blood of those asphyxiated by CO is persistently bright-red in color. When suitably diluted and examined with the spectroscope, it presents an absorption spectrum (No. 6, fig. 37, p. 547) of two bands similar to that of oxyhæmoglobin (No. 3, fig. 37), but in which the two bands are more equal and somewhat nearer the violet end of the spectrum. Owing to the greater stability

of the CO compound, its spectrum may be readily distinguished from that of the O compound by the addition of a reducing agent (an ammoniacal solution of ferrous tartrate), which changes the spectrum of oxyhæmoglobin to the single-band spectrum of hæmoglobin (No. 1, fig. 37), while that of the CO compound remains unaltered, or only fades partially.

If a solution of caustic soda of sp. gr. 1.3 be added to normal blood, a black, slimy mass is formed, which, when spread upon a white plate, has a greenish-brown color. The same reagent added to blood altered by CO forms a firmly clotted mass, which in thin layers upon a white surface is bright red in color.

A piece of gun-cotton upon which platinum-black has been dusted fires in air containing 2.5 in 1,000 of CO.

For the method of determining CO in gaseous mixtures, see p. 309.

**Carbon Dioxid—Carbonic anhydrid—Carbonic acid gas—$CO_2$—44**—is obtained: (1) By burning C in air or O. (2) By decomposing a carbonate (marble=$CaCO_3$) by a mineral acid (HCl diluted with an equal volume of $H_2O$).

At ordinary temperatures and pressures it is a colorless, suffocating gas; has an acidulous taste; sp. gr. 1.529 A; soluble in an equal volume of $H_2O$ at the ordinary pressure, much more soluble as the pressure increases. **Soda water** is a solution of carbonic acid in $H_2O$ under increased pressure. When compressed to the extent of 38 atmospheres at 0° (32° F.); 50 atm. at 15° (59° F.); or 73 atm. at 30° (86° F.) it forms a transparent, mobile liquid, by whose evaporation, when the pressure is relieved, sufficient cold is produced to solidify a portion into a snow-like mass, which, by spontaneous evaporation in air, produces a temperature of —90° (—130° F.).

Carbon dioxid neither burns nor does it support combustion. When heated to 1,300° (2,370° F.), it is dissociated into CO and O. A similar decomposition is brought about by the passage through it of electric sparks. When heated with H it yields CO and $H_2O$, When K, Na, or Mg is heated in an atmosphere of $CO_2$, the gas is decomposed with formation of a carbonate and separation of carbon. When caused to pass through solutions of the hydroxids of Na, K, Ca, or Ba, it is absorbed, with formation of the carbonates of those metals, which, in the case of the last two, are deposited as white precipitates. Solution of potash is frequently used in analysis to absorb $CO_2$, and lime and baryta water as tests for its presence. The hydroxids mentioned also absorb $CO_2$ from moist air.

*Atmospheric Carbon Dioxid.*—Carbon dioxid is a constant constituent of atmospheric air in small and varying quantities; the mean amount in free country air being about 4 in 10,000. On land the amount is greater by night than by day, while the reverse is the case at

sea. On land the green parts of plants absorb $CO_2$ during the hours of sunlight, but not during those of darkness. The increase in the amount in air over large bodies of water during the daytime is due to the less solubility of $CO_2$ in the surface-water when heated by the sun's rays. The absence of vegetation accounts for the large quantity of $CO_2$ in the air of the polar regions, and the same cause, aided by an increased production, for its excess in the air of cities over that of the country.

The sources of atmospheric $CO_2$ are :

(1) The respiration of animals.—The expired air under ordinary conditions contains about 4.5 per cent. by volume of $CO_2$, the proportion being greater the slower the respiration.

(2) Combustion.—The greater part of the atmospheric $CO_2$ is a product of the oxidation of C in some form as a source of light and heat. In equal times, an ordinary gas-burner produces nearly six times as much $CO_2$, and consumes nearly ten times as much air as a man.

(3) Fermentation. — Most fermentations, including putrefactive changes, are attended by the liberation of $CO_2$. Thus, alcoholic fermentation takes place according to the equation :

$$\underset{180}{C_6H_{12}O_6} = \underset{92}{2C_2H_6O} + \underset{88}{2CO_2}$$

and consequently discharges into the air 88 parts by weight of $CO_2$ for every 92 parts of alcohol formed, or 384 litres of gas for every litre of absolute alcohol obtained.

(4) Tellural sources.—Volcanoes in activity discharge enormous quantities of $CO_2$, and, in volcanic countries the same gas is thrown out abundantly through fissures in the earth. All waters, sweet and mineral, hold this gas in solution, and those which have become charged with it under pressure in the earth's crust, upon being relieved of the pressure when they reach the surface, discharge the excess into the air.

(5) Manufacturing processes.—Large quantities of $CO_2$ are added to the air in the vicinity of lime- and brick-kilns, cement-works, etc.

(6) In mines, after explosions of "fire-damp." These explosions are caused by the sudden union of the C and H of $CH_4$, with the O of the air, and are consequently attended by the formation of large volumes of $CO_2$, known to miners as *after-damp*.

*Constancy of the amount of atmospheric carbon dioxid.*—It has been roughly estimated by Poggendorff that 2,500,000,000,000 cubic metres of $CO_2$ are annually discharged into our atmosphere, and that this quantity represents one eighty-sixth of the total amount at present existing therein. This being the case, with the present production,

the percentage of atmospheric $CO_2$ would be doubled in eighty-six years. No such increase has, however, been observed. The $CO_2$ discharged into the air is, therefore, removed from it about as fast as it is produced. This removal is effected in two ways: (1) by the formation of deposits of earthy carbonates by animal organisms, corals, mollusks, etc.; (2) principally by the process of nutrition of vegetables, which absorb $CO_2$ both by their roots and leaves, and in the latter, under the influence of the sun's rays, decompose it, retaining the C, which passes into more complex molecules; and discharging a volume of O about equal to that of the $CO_2$ absorbed.

*Air contaminated with excess of carbon dioxid, and its effects upon the orgdnism.*—When, from any of the above sources, the air of a given locality has received sufficient $CO_2$ to raise the proportion above 7 in 10,000 by volume, it is to be considered as contaminated; the seriousness of the contamination depending not only upon the amount of the increase, but also upon the source of the $CO_2$. If the gas be derived from fermentation, or from tellural or manufacturing sources, it is simply added to the otherwise unaltered air, and the absolute amount of oxygen present remains the same. When, however, it is produced in a confined space by the processes of combustion and respiration, the composition of the air is much more seriously modified, as not only is there addition of a deleterious gas, but a simultaneous removal of an equal volume of O; hence the importance of providing, by suitable ventilation, for the supply of new air from without to habitations and other places where human beings are collected within doors, especially where the illumination is by gas-lights.

Although an adult man deoxidizes a little over 100 litres of air in an hour, a calculation of the quantity which he would require in a given time cannot be based exclusively upon that quantity, as the deoxidation cannot be carried to completeness; indeed, when the proportion of $CO_2$ in air exceeds five per cent, it becomes incapable of supporting life, while a much smaller quantity, one per cent., is provocative of severe discomfort, to say the least.

In calculating the quantity of air which should be supplied to a given enclosed space, most authors have agreed to adopt as a basis that the percentage of $CO_2$ should not be allowed to exceed 0.6 volume per 1,000; of which 0.4 is normally present in air, and 0.2 the product of respiration or combustion. Taking the amount of $CO_2$ eliminated by an adult at 19 litres (=0.7 cubic foot) per hour, a man will have brought the air of an air-tight space of 100 cubic metres (=3,500 cubic feet) up to the permissible maximum of impurity in an hour.

Practically, owing to the imperfect closing of doors and windows, and to ventilation by chimneys, inhabited spaces are never hermeti-

cally closed, and a less quantity of air-supply than would be required in an air-tight space will suffice.

A sleeping-room occupied by a single person should have a cubic space of 30 to 50 cubic metres (=1,050 to 1,800 cubic feet), conditions which are fulfilled in rooms measuring 10×13×8 feet and 13×15.6×9 feet.

In calculating the space of dormitories to be occupied by several healthy people, the smallest air-space that should, under any circumstances, be allowed, is 12 cubic metres (=420 cubic feet) for each person. To determine the number of individuals that may sleep in a room, multiply its length, width and height together, and divide the product by 420 if the measurement be in feet, or by 12 if it be in metres. Thus, a dormitory 40 feet long, 20 feet wide and 10 feet high is fitted for the accommodation of 19 persons at most; for $40\times20\times10=8,000$ and $\frac{8000}{420}=19.05$.

As a rule, in places where many persons are congregated, it is necessary to resort to some scheme of ventilation by which a sufficient supply of fresh air shall be introduced and the vitiated air removed, the quantity to be supplied varying according to circumstances. Experiment has shown that, in order to keep the air pure to the senses, the quantity of air which must be supplied per head and per hour in temperate climates is as shown in the table:

| Situation. | Cubic metres. | Cubic feet. | Situation. | Cubic metres. | Cubic feet. |
|---|---|---|---|---|---|
| Barracks (day time) | 35 | 1,236 | Hospital wards (surgical) | 170 | 6,004 |
| Barracks (night time) | 70 | 2,472 | Contagious and lying-in | 170 | 6,004 |
| Workshops (mechanical) | 70 | 2,472 | Mines, metaliferous | 150 | 5,297 |
| School rooms | 35 | 1,236 | Mines, coal | 170 | 6,004 |
| Hospital wards | 85 | 3,002 | | | |

The amounts given are the smallest permissible, and should be exceeded wherever practicable.

*Lights.*—Each cubic foot of illuminating gas consumes in its combustion a quantity of O equal to that contained in 7.14 cubic feet of air, and produces 0.8 cubic feet of $CO_2$, besides a large quantity of watery vapor, and less amounts of $H_2SO_4$, $SO_2$ and sometimes CO; and an ordinary gas-burner consumes about three feet per hour. It is obvious, therefore, that a much larger quantity of pure air must be furnished to maintain the atmosphere of an apartment at the standard of 0.6 per 10000 of $CO_2$, when the vitiation is produced by the combustion of gas, than when it is the result of the respiration of a human being, and that to such an extent that a single three-foot burner requires a supply of air which would be sufficient for six human beings.

In theaters the contamination of the air by the burning of gas should be entirely eliminated by the use of electricity or by placing the gas-burners either under the dome ventilator, or in boxes which open to the air of the house only below the level of the burner, and which are in communication with a ventilating-shaft.

When artificial illumination is obtained from lamps or candles, or from gas in small quantity and for a short time, the contamination of the air is sufficiently compensated by the ventilation through imperfect closing of the windows. A room without a window should never be used for human habitation.

One important advantage of the electric light is that it consumes no O and produces no $CO_2$.

Although, by the combustion of fuel, O is consumed and $CO_2$ produced, heating arrangements only become a source of vitiation of air when they are improperly constructed. Indeed, in the majority of cases, if properly arranged, they are the means of ventilation, either by aspirating the vitiated air of the apartment, or by the introduction of air from without.

**Action on the Economy.**—An animal introduced into an atmosphere of pure $CO_2$ dies almost instantly, and without entrance of the gas into the lungs, death resulting from spasm of the glottis, and consequent apnœa.

When diluted with air, the action of $CO_2$ varies according to its proportion, and according to the proportion of O present.

When the proportion of O is not diminished, the poisonous action of $CO_2$ is not as manifest, in equal quantities, as when the air is poorer in oxygen. An animal will die rapidly in an atmosphere composed of 21 per cent. O, 59 per cent. N, and 20 per cent. $CO_2$ by volume; but will live for several hours in an atmosphere whose composition is 40 per cent. O, 37 per cent. N, 23 per cent. $CO_2$. If $CO_2$ be added to normal air, of course the relative quantity of O is slightly diminished, while its absolute quantity remains the same. This is the condition of affairs existing in nature when the gas is discharged into the air; under these circumstances an addition of 10–15 per cent. of $CO_2$ renders an air rapidly poisonous, and one of 5–8 per cent. will cause the death of small animals more slowly. Even a less proportion than this may become fatal to an individual not habituated.

When present in large proportion, $CO_2$ produces immediate loss of muscular power, and death without a struggle; when more dilute, a sense of irritation of the larynx, drowsiness, pain in the head, giddiness, gradual loss of muscular power, and death in coma.

If the $CO_2$ present in air be produced by respiration, or combustion, the proportion of O is at the same time diminished, and much smaller absolute and relative amounts of the poisonous gas will

produce the effects mentioned above. Thus, an atmosphere containing in volumes 19.75 per cent. O, 74.25 per cent. N, 6 per cent. $CO_2$, is much more rapidly fatal than one composed of 21 per cent. O, 59 per cent. N, 20 per cent. $CO_2$. With a corresponding reduction of O, 5 per cent. of $CO_2$ renders an air sufficiently poisonous to destroy life; 2 per cent. produces severe suffering; 1 per cent. causes great discomfort, while 0.1 per cent., or even less, is recognized by a sense of closeness.

**The treatment** in all cases of poisoning by $CO_2$ consists in the inhalation of pure air (to which an excess of O may be added), aided, if necessary, by artificial respiration, the cold douche, galvanism, and friction.

**Detection of Carbon Dioxid and Analysis of Confined Air.**—Carbon dioxid, or air containing it, causes a white precipitate when caused to bubble through lime or baryta water. Normal air contains enough of the gas to form a scum upon the surface of these solutions when exposed to it.

It was at one time supposed that air in which a candle continued to burn was also capable of maintaining respiration. This is, however, by no means necessarily true. A candle introduced into an atmosphere in which the normal proportion of O is contained, burns readily in the presence of 8 per cent. of $CO_2$; is perceptibly dulled by 10 per cent.; is usually extinguished with 13 per cent.; always extinguished with 16 per cent. Its extinction is caused by a less proportion of $CO_2$, 4 per cent., if the quantity of O be at the same time diminished. Moreover, a contaminated atmosphere may not contain enough $CO_2$ to extinguish, or perceptibly dim the flame of a candle, and at the same time contain enough of the monoxid to render it fatally poisonous if inhaled.

The presence of $CO_2$ in a gaseous mixture is determined by its absorption by a solution of potash; its quantity either by measuring the diminution in bulk of the gas, or by noting the increase in weight of an alkaline solution.

To determine the proportions of the various gases present in air the apparatus shown in Fig. 36 is used. A is an aspirator of known capacity, filled with water at the beginning of the operation. It connects by a flexible tube from its upper part with an absorbing apparatus consisting of *a*, a U-shaped tube containing fragments of pumice-stone, moistened with $H_2SO_4$; by the increase in weight of this tube the weight of watery vapor in the volume of air drawn through by the aspirator is determined; *b*, a Liebig's bulb filled with a solution of potash; *c*, a U-tube filled with fragments of pumice moistened with $H_2SO_4$; *b* and *c* are weighed together and their increase in weight is the weight of $CO_2$ in the volume of air operated

on. Every gram of increase in weight represents 0.50607 litre, or 31.60356 cubic inches; *d* is a tube of difficultly fusible glass, filled with black oxid of copper and heated to redness; *e* is a **U**-tube filled with pumice moistened with $H_2SO_4$; its increase in weight represents $H_2O$ obtained from decomposition of $CH_4$. Every gram of increase in weight of *e* represents 0.444 gram, or 0.621 litre, or 38.781 cubic inches of marsh-gas; *f* and *g* are similar to *b* and *c*, and their increase

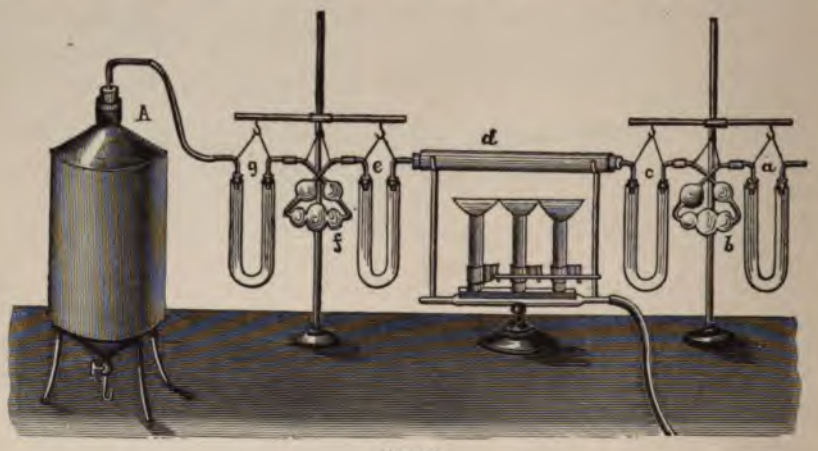



FIG. 36.

in weight represents $CO_2$ formed by oxidation of CO and $CH_4$ in *d*. From this the amount of CO is thus calculated: First, 2.75 grams are deducted from the increase of weight of *f* and *g* for each gram of $CH_4$ found by *e;* of the remainder, every gram represents 0.6364 gram, or 0.5085 litre, or 31.755 cubic inches of CO. The air is drawn through the apparatus by opening the stopcock of A to such an extent that about thirty bubbles a minute pass through *b*.

### ACIDYL ANHYDRIDS.

The acidyl anhydrids of the monobasic acids are produced by the action of the acidyl chlorids upon anhydrous salts: $C_2H_3O.OK + C_2H_3O.Cl = (C_2H_3O)_2O + KCl$; or by the action of phosphorus oxychlorid upon the alkali salts of the acids. In this method of formation the acidyl chlorid is first produced: $2C_2H_3O.OK + POCl_3 = 2C_2H_3O.Cl + PO_3K + KCl$; and this acts upon an excess of the salt according to the above equation.

**Acetic Anhydrid**—$(C_2H_3O)_2O$—is a pungent liquid which boils at 137° (278.6° F.). It is formed by the general methods and also by heating lead acetate with carbon disulfid at 165° (329° F.).

It serves for the introduction of the radical acetyl into other molecules.

Anhydrids of the oxyacids and of the pure dicarboxylic acids also exist.

## ACIDYL HALOIDS.

These compounds, also known as haloid anhydrids, are the halogen compounds of the acidyls. They are produced: (1) by the action of the phosphorus haloids upon the acids or their salts (see above); (2) by the action of phosgene upon the acids, or their salts: $COCl_2 + CH_3.COOH = CH_3.CO.Cl + CO_2 + HCl$; (3) by the action of phosphorus pentoxid upon the acids in presence of hydrochloric acid: $3CH_3.COOH + 3HCl + P_2O_5 = 3CH_3.CO.Cl + 2PO_4H_3$; or (4) by the action of chlorin upon the aldehydes: $Cl_2 + CH_3.CO.H = CH_3.CO.Cl + HCl$.

**Acetyl Chlorid**—$CH_3.CO.Cl$—is a colorless, pungent liquid, which boils at 55° (131° F.) It is decomposed by water with formation of acetic and hydrochloric acids. With acetic acid it forms acetic anhydrid. It is used to produce acetyl derivatives.

## ESTERS—COMPOUND ETHERS.

As the alcohols resemble the mineral bases, and the organic acids resemble those of mineral origin, so the esters are similar in constitution to the salts, being *formed by the double decomposition of an alcohol with an acid, mineral or organic*, as a salt is formed by double decomposition of an acid and a mineral base, the radical playing the part of an atom of corresponding valence:

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| $\left.\begin{matrix}K'\\H\end{matrix}\right\}O$ | + | $\left.\begin{matrix}(NO_2)\\H\end{matrix}\right\}O$ | = | $\left.\begin{matrix}H\\H\end{matrix}\right\}O$ | + | $\left.\begin{matrix}(NO_2)\\K'\end{matrix}\right\}O$ |
| Potassium hydroxid. | | Nitric acid. | | Water. | | Potassium nitrate. |
| $\left.\begin{matrix}(C_2H_5)'\\H\end{matrix}\right\}O$ | + | $\left.\begin{matrix}(NO_2)\\H\end{matrix}\right\}O$ | = | $\left.\begin{matrix}H\\H\end{matrix}\right\}O$ | + | $\left.\begin{matrix}(NO_2)\\(C_2H_5)'\end{matrix}\right\}O$ |
| Ethyl hydroxid (alcohol). | | Nitric acid. | | Water. | | Ethyl nitrate (nitric ether). |

Therefore **the esters are acids whose hydrogen has been partially or completely displaced by a hydrocarbon radical or radicals.**

Some of the esters still contain a portion of the acid hydrogen which, being replaceable by another radical or by a metal, communicates acid qualities to the substance, which is at the same time an ester and a true acid. Or di- and polyhydric alcohols, in combining with acids of inferior basicity, may form esters which still retain alcoholic hydroxyls, and which are, therefore, **alcohol-esters.**

### ESTERS OF THE MONOHYDRIC ALCOHOLS.

These esters are produced:

(1) By the action of the acid upon the alcohol: $H_2SO_4+CH_3.CH_2OH=CH_3.CH_2.HSO_4+H_2O$; or $H_2SO_4+2CH_3.CH_2OH=(CH_3.CH_2)_2SO_4+2H_2O$.

(2) By the action of the corresponding haloid esters upon the silver salt of the acid: $AgNO_3+C_2H_5I=AgI+C_2H_5.NO_3$.

(3) By the action of the acidyl chlorids upon the sodium derivatives of the alcohols, and in some instances upon the alcohols themselves: $C_2H_3O.Cl+C_2H_5.O.Na=NaCl+C_2H_3O_2.C_2H_5$.

All esters are decomposed into acid and alcohol by the action of water at high temperatures, or of caustic potash or soda: $(C_2H_5)NO_3+KHO=KNO_3+C_2H_5HO$.

As this decomposition is analogous to that utilized in the manufacture of soap (p. 318), it is known as **saponification**, and whenever an ester is so decomposed it is said to be **saponified.** When the decomposition is effected by $H_2O$ the free acid and the alcohol are formed, and it is known as **hydrolysis** (p. 70): $(C_2H_5)C_2H_3O_2+H_2O=C_2H_5.HO+H.C_2H_3O_2$.

**Ethyl Nitrate**—*Nitric ether*—$\left.\begin{matrix}NO_2\\C_2H_5\end{matrix}\right\}O$—91.—A colorless liquid; has a sweet taste and bitter after-taste; sp. gr. 1.112 at 17° (62.6° F.); boils at 85° (185° F.); gives off explosive vapors. Prepared by distilling a mixture of $HNO_3$ and $C_2H_6O$ in the presence of urea.

**Ethyl Nitrite**—*Nitrous ether*—$\left.\begin{matrix}NO\\C_2H_5\end{matrix}\right\}O$—75—is prepared by directing nitrous fumes into alcohol, contained in a retort connected with a well-cooled receiver.

It is a yellowish liquid; has an apple-like odor, and a sharp, sweetish taste: sp. gr. 0.947; boils at 18° (64.4° F.); gives off inflammable vapor; very sparingly soluble in $H_2O$; readily soluble in alcohol and ether. It is decomposed by warm $H_2O$, by alkalies, by $H_2SO_4$, $H_2S$, and the alkaline sulfids, and is liable to spontaneous decomposition, especially in the presence of $H_2O$. Its vapor produces anæsthesia, and it exists in alcoholic solution in **Spiritus ætheris nitrosi** (U. S.; Br.).

**Ethyl Sulfates**—$(C_2H_5)HSO_4$=*Ethyl sulfuric* or *sulfovinic acid* and $(C_2H_5)_2SO_4$—*Ethyl sulfate*—*Sulfuric ether.*

**Ethyl-sulfuric Acid**—$\begin{matrix}C_2H_5.O\\HO\end{matrix}\!\!>\!SO_2$—is formed as an intermediate product in the manufacture of ethylic ether (p. 300). It is a colorless, syrupy, highly acid liquid; sp. gr. 1.316; soluble in water and alcohol in all proportions, insoluble in ether.

It decomposes slowly at ordinary temperatures, more rapidly when heated. When heated with alcohol, it yields ethylic ether and $H_2SO_4$.

When heated with $H_2O$, it yields alcohol and $H_2SO_4$. It forms crystalline salts, known as **sulfovinates**, or **sulfethylates**, one of which, **sodium sulfovinate** $(C_2H_5)NaSO_4$, has been used in medicine. It is a white, deliquescent solid; soluble in $H_2O$.

**Ethyl Sulfate** — $(C_2H_5)_2SO_4$—the true sulfuric ether, is obtained by passing vapor of $SO_3$ into *pure* ethylic ether, thoroughly cooled. It is a colorless, oily liquid; has a sharp, burning taste, and the odor of peppermint; sp. gr. 1.120. It cannot be distilled without decomposition. With $H_2O$ it forms sulfovinic acid.

**Sulfurous and Hyposulfurous Esters.**—These compounds have recently assumed medical interest from their relationship to mercaptan, sulfonal and a number of aromatic derivatives used as medicines.

There exist two isomeric sulfurous acids (p. 97), both of which yield neutral esters, but only one of which, the unsymmetrical, $\begin{matrix}O\\O\end{matrix}\!\!\diagdown\!\!\diagup\!S\!\!<\!\!\begin{matrix}H\\OH\end{matrix}$, forms acid esters. These acid esters are known as **sulfonic acids.** (See Aromatic sulfonic acids, mercaptan, sulfones, sulfonal.)

**Diethyl Sulfite**—$(C_2H_5)_2SO_3$—is produced by the action of thionyl chlorid on absolute alcohol: $SOCl_2+2C_2H_5HO=SO_3(C_2H_5)_2+2HCl$. It is a colorless liquid, having a powerful odor: sp. gr. 1.085, boils at 161° (321.8° F.). $H_2O$ decomposes it into alcohol and sulfurous acid.

**Ethyl Sulfonic Acid**—$SO_2\!<\!\begin{matrix}C_2H_5\\OH\end{matrix}$—is formed by the action of ethyl iodid on potassium sulfite: $C_2H_5I+SO_3K_2=C_2H_5.SO_2OK+KI$. It forms salts and esters.

**Sulfinic Acids** — are the acid esters of hyposulfurous acid $SO\!<\!\begin{matrix}H\\OH,\end{matrix}$ and are analogous to the sulfonic acids.

**Ethyl Acetate** — **Acetic ether** — **Æther aceticus** — (U. S.) — $\left.\begin{matrix}C_2H_3O\\C_2H_5\end{matrix}\right\}O$—is obtained by distilling a mixture of sodium acetate, alcohol and $H_2SO_4$; or by passing carbon dioxid through an alcoholic solution of potassium acetate.

It is a colorless liquid, has an agreeable, ethereal odor: boils at 74° (165.2° F.); sp. gr. 0.89 at 15° (59° F.); soluble in 6 pts. water, and in all proportions in methyl and ethyl alcohols and in ether; a good solvent of essences, resins, cantharidin, morphin, gun cotton, and in general, of substances soluble in ether; burns with a yellowish-white flame. Chlorin acts energetically upon it, producing products of substitution, varying according to the intensity of the light from $C_4H_6Cl_2O_2$ to $C_4Cl_8O_2$.

**Ethyl Aceto-acetate** — **Aceto-acetic ester** — $CH_3.CO.CH_2.COO(C_2H_5)$—is the most important representative of the class of $\beta$-ketonic acid esters (p. 298), which are important synthetic reagents. It is

prepared by dissolving 6 pts. of metallic sodium in 200 pts. of anhydrous ethyl acetate, distilling off the excess of the ester, mixing the residue with 50% acetic acid in slight excess, decanting the oil which separates, and fractioning.

The formation of aceto-acetic ester in this process occurs in several reactions, the sum of which may be expressed by the equation: $2CH_3.COO(C_2H_5) = CH_3.CO.CH_2.COO(C_2H_5) + CH_3.CH_2OH$; two molecules of ethyl acetate forming one molecule of aceto-acetic ester and one of ethylic alcohol. In one stage of the reaction sodium acts upon ethyl acetate to form ethyl acetyl-sodacetate, sodium ethylate and hydrogen: $2CH_3.COO(C_2H_5)+Na_2=CH_3.CO.CHNa.COO(C_2H_5)-+C_2H_5.O.Na+H_2$. In another, sodium ethylate acts upon ethyl acetate to form ethyl acetyl-sodacetate and ethylic alcohol: $2CH_3.COO(C_2H_5) + C_2H_5.O.Na = CH_3.CO.CHNa.COO(C_2H_5) + 2CH_3.CH_2OH$; and, when the operation is properly conducted, little or no hydrogen is evolved, because that produced in the above reaction acts with sodium upon ethyl acetate to form sodium ethylate: $CH_3.COO(C_2H_5)+Na_2+H_2=2C_2H_5.O.Na$. The aceto-acetic ester is liberated from its sodium derivative by acetic acid: $CH_3.CO.CHNa.COO(C_2H_5)+CH_3.COOH=CH_3.COONa+CH_3.CO.CH_2.COO(C_2H_5)$.

Other esters of $\beta$-ketonic acids are derived from ethyl acetyl-sodacetate by the action of alkyl iodids. Thus: $CH_3.CO.CHNa.COO(C_2H_5)+CH_3I=CH_3.CO.CH(CH_3).COO(C_2H_5)+NaI$; then, $2CH_3.CO.CH.(CH_3).COO(C_2H_5)+Na_2 = 2CH_3.CO.CNa(CH_3).COO(C_2H_5)-+H_2$; and $CH_3.CO.CNa(CH_3).COO(C_2H_5) + CH_3I = CH_3.CO.C(CH_3)_2.COO(C_2H_5)+NaI$.

Heating with dilute alkalies decomposes the $\beta$-ketonic esters, with formation, either of ketones: $CH_3.CO.CH_2.COO(C_2H_5)+2KHO=CH_3.CO.CH_3+CO_3K_2+C_2H_5.OH$; or of acetates and salts of higher acids of the same series: $CH_3.CO.CH(CH_3).COO(C_2H_5)+2KHO=CH_3.COOK+CH_3.CH_2.COOK+C_2H_5.OH$. Nascent hydrogen converts them into the corresponding $\beta$-oxy-acids. Thus ethyl aceto-acetate yields ethyl $\beta$-oxy-butyrate: $CH_3.CO.CH_2.COO(C_2H_5)+H_2=CH_3.CHOH.CH_2.COO(C_2H_5)$.

Acetyl-acetic ester is utilized in a great number of syntheses of both aromatic and aliphatic compounds. It is a colorless liquid, b. p. 181° (357.8° F.), having a pleasant odor, and almost insoluble in water. It is colored violet by ferric chlorid.

**Amyl Nitrate**—$C_5H_{11}\}^{NO_2}O$—obtained by distilling a mixture of $HNO_3$ and amylic alcohol in the presence of a small quantity of urea. It is a colorless, oily liquid; sp. gr. 0.994 at 10° (50° F.); boils at 148° (298.4° F.) with partial decomposition.

**Amyl Nitrite—Amyl nitris** (U. S.)—$C_5H_{11}\}^{NO}O$—117—prepared

by directing nitrous fumes into amyl alcohol, contained in a retort heated over a water-bath; purifying the distillate by washing with an alkaline solution, and rectifying.

It is a slightly yellowish liquid; sp. gr. 0.877; boils at 95° (203° F.). Its vapor, which is orange-colored, explodes when heated to 260° (500° F.). It is insoluble in water; soluble in alcohol in all proportions. Alcoholic solution of potash decomposes it slowly, with formation of potassium nitrite and ethyl and amyl oxids. When dropped upon fused potash, it ignites and yields potassium valerianate.

**Amyl Acetate—Pear oil**—$\left.\begin{matrix}C_2H_3O\\C_5H_{11}\end{matrix}\right\}O$—is prepared by distilling a mixture of sulfuric acid, amylic alcohol and potassium acetate. It has the odor of pears, is insoluble in water, soluble in alcohol; and boils at 125° (257° F.). It is used as a flavoring agent and as a solvent for celluloid.

**Cetyl Palmitate—Cetin**—$\left.\begin{matrix}C_{16}H_{31}O\\C_{16}H_{33}\end{matrix}\right\}O$—480—is the chief constituent of **spermaceti=cetaceum** (U. S., Br.), which, besides cetin, contains esters of palmitic, stearic, myristic, and laurostearic acids; and of the alcohols: **lethol**, $C_{12}H_{26}O$; **methol**, $C_{14}H_{30}O$; **ethol**, $C_{16}H_{34}O$, and **stethol**, $C_{18}H_{38}O$.

**Melissyl Palmitate** — *Melissin*—$\left.\begin{matrix}C_{16}H_{31}O\\C_{30}H_{61}\end{matrix}\right\}O$—676.—Beeswax consists mainly of two substances: **cerotic acid**, $C_{27}H_{53}O.OH$, which is soluble in boiling alcohol, and **melissyl palmitate**, insoluble in that liquid, united with minute quantities of substances which communicate to the wax its color and odor. Yellow wax melts at 62°–63° (143.6°–145.4° F.). After bleaching, which is brought about by exposure to light, air, and moisture, it does not fuse below 66° (150.8° F.). **China wax**, a white substance resembling spermaceti, is a vegetable product, consisting chiefly of **ceryl cerotate**, $C_{27}H_{53}O_2(C_{27}H_{55})$.

## ESTERS OF DIHYDRIC ALCOHOLS OR GLYCOLS.

The glycols behave as diacid bases and form with the monobasic acids basic and also neutral esters:

| | | |
|---|---|---|
| $CH_2OH$ | $CH_2.OOC.CH_3$ | $CH_2OOC.CH_3$ |
| $CH_2OH$ | $CH_2OH$ | $CH_2.OOC.CH_3$ |
| Glycol. | Glycol mono-acetate. | Glycol diacetate. |

The **haloid esters** of the glycols are also basic or neutral. The basic compounds are the **glycol halohydrins**, e. g., $CH_2OH.CH_2Cl$= **Ethylene chlorhydrin**, produced by the action of the hydracids upon the glycols, or upon ethylene oxid and its homologues.

The neutral haloid esters are among the haloid derivatives of the

paraffins, higher than the first (pp. 233–237). They are produced by (1) the substitution of the halogen in the paraffin or in the monohalogen paraffin; thus ethyl chlorid: $CH_3.CH_2Cl$ yields ethylene chlorid; $CH_2Cl.CH_2Cl$; (2) by addition of the halogens to the olefins (p. 368), thus ethylene: $CH_2:CH_2$ yields ethylene bichlorid; $CH_2Cl.CH_2Cl$; (3) by the action of the hydracids upon the monohalogen olefins, or upon the glycols, or upon the glycol chlorhydrins. Thus ethylene bichlorid is obtained from ethylene monochlorid: $CHCl:CH_2$; ethylene glycol: $CH_2OH.CH_2OH$; or ethylene chlorhydrin: $CH_2OH.CH_2Cl$. By this latter method two isomeres: $CHCl_2.CH_3$ and $CH_2Cl.CH_2Cl$ may be produced.

The neutral haloid esters of the glycols are the starting points in the preparation of the glycols: $CH_2Br.CH_2Br+2AgHO=2AgBr+CH_2OH.CH_2OH$. Nascent hydrogen converts them into the paraffins: $CH_2Cl.CH_2Cl+2H_2=2HCl+CH_3.CH_3$.

**Ethylene Chlorid—Elayl chlorid—Dutch liquid**—$CH_2Cl.CH_2Cl$—is obtained by passing ethylene through a retort in which chlorin is generated. It is a colorless, oily liquid, has a sweetish taste and an ethereal odor; boils at 84° (183.2° F.). It is capable of fixing other atoms of chlorin by substitution to form a series of compounds, the most highly chlorinated of which is **carbon trichlorid**, $C_2Cl_6$.

### ESTERS OF THE TRIHYDRIC ALCOHOLS OR GLYCEROLS—GLYCERIDS.

The glycerols behave as triacid bases, forming three series of esters with the monobasic acids. These esters are the **mono-**, **di-**, and **triglycerids**. Moreover, as two of the hydroxyls of the alcohol are in the primary groups $CH_2OH$, while the third is in the secondary group, CHOH, there are two isomeres of each mono- and diglycerid:

| | | | | |
|---|---|---|---|---|
| $CH_2.C_2H_3O_2$ | $CH_2OH$ | $CH_2.C_2H_3O_2$ | $CH_2.C_2H_3O_2$ | $CH_2.C_2H_3O_2$ |
| CHOH | $CH.C_2H_3O_2$ | CHOH | $CH.C_2H_3O_2$ | $CH.C_2H_3O_2$ |
| $CH_2OH$ | $CH_2.OH$ | $CH_2.C_2H_3O_2$ | $CH_2OH$ | $CH_2.C_2H_3O_2$ |
| α-Monacetin. | β-Monacetin. | α-Diacetin. | β-Diacetin. | Triacetin. |

The haloid esters are known as the **glycerol halohydrins**. Of the glycerol esters of mineral oxyacids those of nitric and phosphoric acids are of interest.

**Trinitroglycerol—Nitroglycerine—Glonoin**—$C_3H_5(NO_3)_3$—is formed by the action of a mixture of $H_2SO_4$ and $HNO_3$ upon glycerol. It is an odorless, yellowish oil; has a sweetish taste; sp. gr. 1.6; insoluble in water, soluble in alcohol and in ether; not volatile; crystallizes in prismatic needles when kept for some time at 0° (32° F.); fuses again at 8° (46.4° F.). When suddenly heated, or when sub-

jected to shock it is explosively decomposed into $CO_2$; N; $H_2O$ and O. Alkalies saponify it to glycerol and nitric acid.

Nitroglycerol is mixed with diatomaceous earth and with other inert, absorbent substances in dynamite and in other high explosives; and, combined with nitrocellulose, it forms "smokeless powder."

It is used in medicine as a cardiac stimulant, and, in overdose, is an active poison, producing effects somewhat similar to those caused by strychnin.

**Glycero-phosphoric Acid**—$C_3H_5(OH)_2.O.PO_3H_2$—is the monoglycerid of phosphoric acid. It is a product of decomposition of the lecithins, or phosphorized fats (p. 319), or may be formed by mixing glycerol and metaphosphoric acid. It is a thick syrup, which is decomposed into glycerol and phosphoric acid when heated with water. It is a dibasic acid.

**Glycerol Esters of Organic Acids.**—The triacid glycerol esters of the acids of the acetic and acrylic series containing an even number of carbon atoms occur in the animal and vegetable fats and oils.

**Tributyrin**—$C_3H_5(O.C_4H_7O)_3$—302—exists in butter. It may also be obtained by heating glycerol with butyric acid and $H_2SO_4$. It is a pungent liquid, very prone to decomposition, with liberation of butyric acid.

**Tricaproïn**—$C_3H_5(O.C_6H_{11}O)_3$—386—**Tricaprylin**—$C_3H_5(O.C_8H_{15}O)_3$—470—and **Tricaprin**—$C_3H_5(O.C_{10}H_{19}O)_3$—554—exist in small quantities in milk, butter, and cocoa butter.

**Tripalmitin**—$C_3H_5(O.C_{16}H_{31}O)_3$—806—exists in most animal and vegetable fats, notably in palm oil. It may also be obtained by heating glycerol with 8 to 10 times its weight of palmitic acid for 8 hours at 250° (482° F.). It forms crystalline plates, very sparingly soluble in alcohol, even when boiling; very soluble in ether. It fuses at 50° (122° F.), and solidifies again at 46° (114.8° F.).

**Trimargarin**—$C_3H_5(O.C_{17}H_{33}O)_3$—848—has probably been obtained artificially as a crystalline solid, fusible at 60° (140° F.), solidifiable at 52° (125.6° F.). The substance formerly described under this name as a constituent of animal fats is a mixture of tripalmitin and tristearin.

**Tristearin**—$C_3H_5(O.C_{18}H_{35}O)_3$—890—is the most abundant constituent of the solid fatty substances. It is prepared in large quantities as an industrial product in the manufacture of stearin candles, etc., but is obtained free from tripalmitin only with great difficulty.

In as pure a form as readily obtainable, it forms a hard, brittle, crystalline mass; fusible at 68° (154.4° F.), solidifiable at 61° (141.8° F.); soluble in boiling alcohol, almost insoluble in cold alcohol, readily soluble in ether.

**Triolein**—$C_3H_5(O.C_{18}H_{33}O)_3$—884—exists in varying quantity in all fats, and is the predominant constituent of those which are liquid at ordinary temperatures. It may be obtained from animal fats by boiling with alcohol, filtering the solution, decanting after twenty-four hours' standing; freezing at 0° (32° F.), and expressing.

It is a colorless, odorless, tasteless oil; soluble in alcohol and ether, insoluble in water; sp. gr. 0.92.

The **Neutral Oils** and **Fats** are mixtures in varying proportions of the triglycerids of the acids of the acetic and acrylic series, principally tripalmitin, tristearin, and triolein. The first two of these are solid at the ordinary temperature and the last liquid. In the oils the last predominates, in the fats the former. In the cold the oils become solid (fats), and, on heating, the fats become oils. The fats and oils are usually odorless, white or yellow, unctuous to the touch, and produce a translucent stain upon paper. They are insoluble in and lighter than water, readily soluble in ether, petroleum ether, benzene, and many other organic solvents. Although the oils do not mix with water, and promptly rise to its surface after having been agitated with it, an oil may remain suspended for a long time; suspended in very minute globules in an aqueous liquid, if bile, pancreatin, albumen, or other **emulsifying agents** be present. Such a mixture, sometimes practically permanent, is called an **emulsion.**

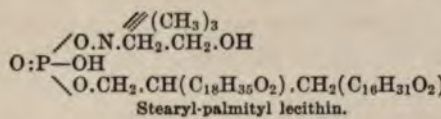
Like other esters the fats and oils are hydrolyzed or saponified when heated with steam or with a caustic alkali. The alcohol, glycerol, is liberated, and, if steam be used, the fatty acid also; while if an alkali be used a **soap** is formed, which is a salt of the fatty acid. The sodium soaps are hard, those of potassium soft. Castile soap is a sodium soap, made from olive oil. Yellow soap is made from tallow or other animal fat, and contains about one-third of its weight of rosin. Lead plaster is lead soap.

The **fixed oils** are so called to distinguish them from the **volatile oils,** more properly called **essences,** which are also unctuous to the touch, and render paper translucent, but which are hydrocarbons, not esters.

The vegetable oils form three classes: (1) The **non-drying, or greasy oils,** which remain liquid and greasy on exposure to air. Olive oil and peanut oil are representatives of this class. (2) **Drying oils,** which dry and become hard when exposed to air. These oils, which contain linoleic acid (p. 375), are used in making paints. Linseed, hemp, poppy, and sunflower oils are drying oils. (3) **Semi-drying oils** are intermediate between the other two classes, and are more or less drying. In this class are cottonseed, sesame, rape seed, and castor oils. The animal oils, used for dressing leather, as lubricants and for illumination, are fish oils, whale, and porpoise oil,

neat's foot oil, lard oil, and tallow oil. **Cod liver oil** contains, besides the glycerids of oleic, myristic, palmitic, and stearic acids, small quantities of those of butyric and acetic acids. It also contains certain biliary principles, a phosphorized fat, traces of iodin and bromin, probably in organic combination, a peculiar fatty acid called **gadinic acid**, a brown substance called **gadinin**, and two alkaloidal bodies: **asellin**, $C_{25}H_{32}N_4$, and **morrhuin**, $C_{19}H_{27}N_3$. **Sperm oil** is not a true oil, but a liquid wax; it contains no glycerids, but consists mainly of esters of the higher monoatomic alcohols.

**Lecithins — Phosphorized Fats.**—These substances are widely distributed in animal and vegetable tissues and fluids, and are particularly abundant in the yolks of eggs, brain, and nerve tissue, semen, and blood-corpuscles and plasma, where they probably serve as material for the formation of the more complex phosphorized bodies such as protagon and the nucleins. The lecithins are colorless or yellowish, imperfectly crystalline solids, of a waxy consistency, and very hygroscopic. They do not dissolve in water, but swell up in it like starch. They are soluble in chloroform, in benzene, and in hot alcohol and hot ether. From alcoholic solutions they crystallize in fine needles. When heated with baryta water or with acids they are decomposed into glycero-phosphoric acid (p. 317), cholin (p. 330), and a fatty acid, usually palmitic or stearic. The lecithins are therefore derivatives of glycero-phosphoric acid, in which the two remaining hydroxyls of the glycerol are replaced by fatty acid residues, and one of the two remaining basic hydrogen atoms of the phosphoric acid is replaced by the basic radical of cholin, which is a quarternary ammonium:



Stearyl-palmityl lecithin.

From the above formula it will be seen that the lecithins may unite with acids, through the remaining OH of the cholin, or with bases, through the remaining basic H of the phosphoric acid, to form salts. The lecithins differ from each other in the nature of the fatty acids entering into their composition. Distearyl-, dioleyl- and stearyl-palmityl lecithins are known.

## ESTERS OF POLYHYDRIC ALCOHOLS, AND OF ALDO- AND KETO-ALCOHOLS

The superior alcohols form esters with the pure acids in the same manner as does glycerol. **Tetra-acetyl erythrol:** $C_4H_6(C_2H_3O_2)_4$, **Tetra-nitro erythrol:** $C_4H_6(NO_3)_4$; **Hexacetyl mannitol:** $C_6H_8$-

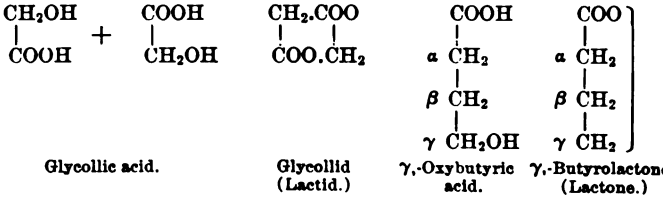
$(C_2H_3O_2)_6$, and **Hexanitro mannitol**: $C_6H_8(NO_3)_6$ are examples of such compounds.

The hexoses also form esters with mineral and organic acids. Thus **diacetic glucose**, $C_6H_{10}O_4(CO_2.CH_3)_2$, is formed as a very bitter solid, very soluble in water, alcohol and ether, by the action of acetic anhydrid upon glucose. This, heated with acetic anhydrid at 140°, furnishes **triacetic glucose**, $C_6H_9O_3(CO_2.CH_3)_3$, which, in turn, is converted into **tetracetic glucose**, $C_6H_8O_2(CO_2.CH_3)_4$, by the action of acetic anhydrid at 160°.

**Acetochlorhydrose**—$CHO.(CH.CO_2.CH_3)_4.CH_2Cl$—is formed by heating d-glucose with acetyl chlorid: $C_6H_{12}O_6+4C_2H_3O.Cl=C_{14}H_{19}O_9Cl+3HCl+H_2O$. It is a colorless, odorless, bitter semi-solid, insoluble in water, soluble in alcohol and in ether. It reduces Fehling's solution. Heated in presence of water, it regenerates glucose. Heated with potassium phenate, it forms glucosyl phenate, or phenol-glucosid, $CHO.(CH.CO_2.CH_3)_4.CH_2Cl+C_6H_5.O.K.+4H_2O=CHO.(CHOH)_4CH_2.O.C_6H_5+KCl+4CH_3.COOH$, the simplest of the **glucosids**, substances frequently referred to as esters of glucose, but which are more properly composite ethers containing glucose and phenolic residues, united by oxygen (p. 409).

### ESTERS OF OXYACIDS—LACTIDS AND LACTONES.

The oxyacids not only form esters with the alcohols in the same manner as the pure acids, but, being themselves both alcohol and acid, they produce cyclic esters, in the formation of which they play the part of alcohol as well as that of acid. The **lactids** are formed by the interaction of two oxyacid molecules, each performing the functions of both alcohol and acid. The **lactones**, which are formed only by the γ and higher oxyacids, are produced from a single molecule of the acid, whose carboxyl and alcoholic groups interact with each other. The following formulæ will indicate the genesis of the lactids and lactones:




Glycollic acid. Glycollid (Lactid.) γ,-Oxybutyric acid. γ,-Butyrolactone (Lactone.)

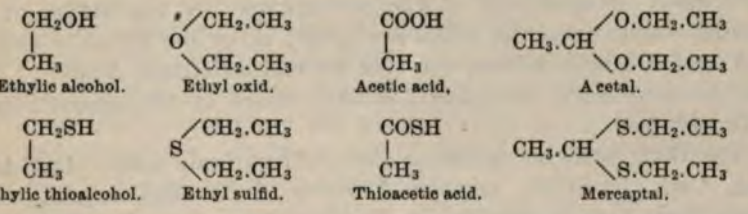
The γ lactones are formed from the γ monohalogen acids: (1) by distillation: $COOH.CH_2.CH_2.CH_2Cl=\overline{COO.CH_2.CH_2.CH_2}+HCl$; (2) by boiling with $H_2O$, KHO or $K_2CO_3$: $COOH.CH_2.CH_2.CH_2Cl+KHO=H_2O+KCl+\overline{COO.CH_2.CH_2.CH_2}$.

By reduction the higher lactones yield aldo-hexoses. Thus d-glucose is produced by the reduction of the lactone of d-gluconic acid: $\overline{COO.(CHOH)_4.CH_2}+H_2=CHO.(CHOH)_4.CH_2OH$. The higher oxycarboxylic acids readily lose water and are converted into lactones (p. 294).

## SULFUR DERIVATIVES OF THE PARAFFINS

As the mineral sulfids and sulfhydrates correspond to the oxids and hydoxids, so there exist **thioethers** and **thioalcohols**, which are the counterparts of the simple ethers and of the alcohols, as well as **thioaldehydes, thioketones** and **thioacids.** Moreover, as sulfur may be quadrivalent or hexavalent, as well as bivalent, there exist other important compounds, the **sulfoxids, sulfones** and **sulfonic acids,** which have no oxygen analogues.

The following formulæ will serve to illustrate the relations of the oxygen and thio compounds:




**Thioethers, or Sulfids** — are produced by processes corresponding to those by which the ethers are formed: (1) by distilling salts of ethyl-sulfuric acids with potassium sulfid; (2) by the action of the paraffin haloids upon potassium sulfid; and by other methods. They are colorless liquids, having very disagreeable odors.

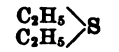
**Thioalcohols—Mercaptans**—are formed by the action of the paraffin haloids upon potassium sulfhydrate: $C_2H_5Cl+KHS=C_2H_5.SH+KCl$; also by distilling the salts of acid sulfuric esters with potassium sulfhydrate: $SO_4.C_2H_5.K+KHS=C_2H_5.SH+K_2SO_4$. The name *mercaptan* (*mercurium captans*) is derived from the property of these compounds of forming a sparingly soluble, crystalline compound with mercuric oxid $(C_2H_5.S)_2Hg$. Such metallic compounds of mercaptan are called **mercaptids.**

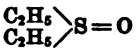
**Ethyl mercaptan — Ethyl sulfhydrate — Thioalcohol**—$CH_3.CH_2.SH$—is prepared industrially, as the first step in the formation of sulfonal, by the first of the general methods given above. It is a colorless liquid, sp. gr. 0.3325, boils at 36.2° (97.2° F.), has an intensely disagreeable odor, burns with a blue flame, is neutral in

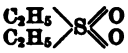
reaction, sparingly soluble in water, soluble in alcohol and in ether, dissolves I, S and P. Potassium and sodium act upon mercaptan as they do upon alcohol, replacing the extra-radical hydrogen to produce mercaptids, or thioethylates, corresponding to the ethylates.

There also exist mono- and di-thioglycols, corresponding to the dihydric alcohols (p. 251). One of these, monothioethylene glycol: $C_2H_4.OH.SH$, yields isethionic acid on oxidation (see below).

**Sulfoxids** and **Sulfones** — are products of oxidation of the sulfids, in which the sulfur is quadrivalent or hexavalent:


Ethyl sulfid.


Ethyl sulfoxid.


Ethyl sulfone.

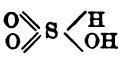
Other products of oxidation of thio-compounds, containing the group $(SO_2)''$ attached to a hydrocarbon group, are also called sulfones (see below).

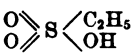
**Sulfonic Acids** — are acids containing the group $(O_2S.OH)'$ attached to a hydrocarbon group. The sulfonic acids of this series are formed by oxidation of the mercaptans; by the action of the paraffin iodids upon the alkaline sulfites; or by the action of sulfuric acid upon alcohols, ethers, etc. (see Aromatic Sulfonic Acids). They may be considered as being the acid esters of the unsymmetrical sulfurous acid.

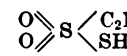
The thioglycols on oxidation also yield sulfonic acids. **Isethionic acid**, $C_2H_4.OH.SO_3H$, mentioned above, is a thick liquid, whose amido derivative is taurin (see Amido-acids).

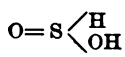
In the **thiosulfonic acids**, which only exist in their salts and esters, the oxygen in the hydroxyl of the sulfonic acids is replaced by sulfur.

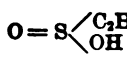
**Sulfinic acids** bear the same relation to hydrosulfurous acid that the sulfonic acids do to the unsymmetrical sulfurous acid:


Unsymmetrical sulfurous acid.

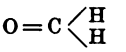

Ethyl sulfonic acid.

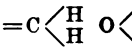

Ethyl thiosulfonic acid.

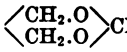

Hydrosulfurous acid.

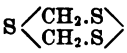

Ethyl sulfinic acid.

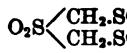
**Thioaldehydes and their Sulfones.**—The simple thioaldehydes are not known, owing to the tendency to polymerize which they possess to a still more marked degree than the aldehydes (p. 257). The trithioaldehydes and their sulfones are known as odorless, colorless solids. The relations of these compounds are shown by the following formulæ:


Formic aldehyde.

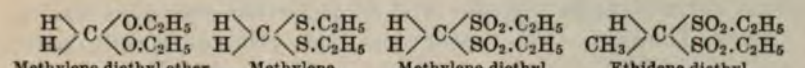

Thioformic aldehyde.


Triform-aldehyde.


Trithioform-aldehyde.


Trimethylene trisulfone.

**Thioacetals—Mercaptals**—are produced by the action of paraffin iodids upon alkali mercaptids, or by the action of HCl upon a mixture of aldehyde and mercaptan. By oxidation they yield sulfones, whose methylene hydrogen may be replaced by alkyl groups :



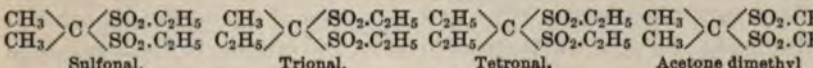

Methylene diethyl ether (Acetal). Methylene mercaptal. Methylene diethyl sulfone. Ethidene diethyl sulfone.

**Thioketones—Mercaptols, and their Sulfones**—are produced by the action of HCl upon a mixture of ketone and mercaptan; or upon an alkyl thiosulfate. In these compounds both of the hydrogen atoms of the methylene group are replaced by alkyl groups. Oxidizing agents convert them into sulfones, among which are sulfonal and its congeners.

**Ethyl Mercaptol**—$(CH_3)_2:C:(SC_2H_5)_2$—is obtained as one of the steps in the manufacture of sulfonal, by the action of dry HCl upon a mixture of acetone and sodium ethylthiosulfate, $C_2H_5S.SO_3Na$. It is a mobile liquid, of not unpleasant odor, boiling at 190° (374° F.).

**Sulfonal—Acetone Diethyl Sulfone**—$(CH_3)_2:C:(SO_2C_2H_5)_2$—is obtained by oxidizing ethyl mercaptol by potassium permanganate. It crystallizes in thick, colorless prisms, difficultly soluble in cold water or alcohol, readily soluble in hot water or alcohol, and in ether, benzene, and chloroform. It fuses at 126° (226.8° F.) and boils at 300° (572° F.), suffering partial decomposition.

Sulfonal contains two ethyl groups, **trional** contains three, and **tetronal** four. Their hypnotic power increases with the number of ethyl groups which they contain. Other "sulfonals" are obtainable from the corresponding mercaptols by methods similar to the above. Among these is **acetone dimethyl sulfone**, which contains no ethyl group, and has no hypnotic action. The relations of these compounds is shown by the following formulæ :




Sulfonal. Trional. Tetronal. Acetone dimethyl sulfone.

**Ichthyol.**—is the Na salt of a complex sulfonic acid, having the empirical formula $C_{28}H_{36}S_3O_6Na_2$, obtained by the distillation and purification of an ozocerite (a mineral pitch). It is a dark brown, pitchlike mass, having a disagreeable odor, soluble in water and in glycerol.

**Thioacids and their Thioanhydrids.**—In the thioacids of the acetic series the sulfur is substituted for the oxygen in the hydroxyl. **Thioacetic acid**, $CH_3.CO.SH$, is formed by the action of phosphorus pentasulfid upon acetic acid.

**Thioacids derivable from Carbonic acid.**— Five of these compounds are known in their derivatives, although the free acids are unknown or very unstable. The formulæ of the free acids are: $CO\langle^{SH}_{OH}$, $CO\langle^{SH}_{SH}$, $CS\langle^{OH}_{OH}$, $CS\langle^{SH}_{OH}$, and $CS\langle^{SH}_{SH}$.

Thio derivatives of glycollic and of lactic acid are also known.

**Carbon Disulfid** — $CS_2$ — bears the same relation to sulfothiocarbonic acid, $CS\langle^{SH}_{OH}$, and to trithiocarbonic acid, $CS\langle^{SH}_{SH}$, that carbon dioxid bears to carbonic acid (p. 302). It is prepared by passing vapor of S over C heated to redness, is partly purified by rectification, and obtained pure by redistillation over mercuric chlorid.

It is a colorless liquid. When pure it has a peculiar, but not disagreeable odor, the nauseating odor of the commercial product being due to the presence of another sulfurated body; boils at 47° (116.6° F.); sp. gr. 1.293; very volatile. Its rapid evaporation in vacuo produces a cold of —60° (—76° F.). It does not mix with $H_2O$. It refracts light strongly.

It is highly inflammable, and burns with a bluish flame, giving off $CO_2$ and $SO_2$; its vapor forms highly explosive mixtures with air, which detonate on contact with a glass rod heated to 250° (482° F.). Its vapor forms a mixture with nitrogen dioxid, which, when ignited, burns with a brilliant flame, rich in actinic rays.

A substance also exists, intermediate in composition between $CO_2$ and $CS_2$, known as **carbon oxysulfid**, CSO, which is an inflammable, colorless gas, obtained by decomposing potassium thiocyanate with dilute $H_2SO_4$.

**Toxicology.**— Cases of acute poisoning by $CS_2$ have hitherto only been observed in animals. Its action is very similar to that of chloroform.

Workmen engaged in the manufacture of $CS_2$, and in the vulcanization of rubber, as well as others exposed to the vapor of the disulfid, are subject to a form of chronic poisoning which may be divided into two stages. The first, or stage of excitation, is marked by headache, vertigo, a disagreeable taste, and cramps in the legs. The patient talks, laughs, sings, and weeps immoderately, and sometimes becomes violently delirious. In the second stage the patient becomes sad and sleepy, sensibility diminishes, sometimes to the extent of complete anæsthesia, especially of the lower extremities, the headache becomes more intense, the appetite is greatly impaired, and there is general weakness of the limbs, which terminates in paralysis.

The only remedy which has been suggested is thorough ventilation of the workshops, and abandonment of the trade at the first appearance of the symptoms.

## ORGANO-METALLIC COMPOUNDS.

These are compounds of the alcoholic radicals with metals. They are usually obtained by the action of the alkyl iodid upon the metallic element, in an atmosphere of H or of $CO_2$. Zinc methid and ethid are valuable synthetic reagents, as in the formation of hydrocarbons, alcohols, and ketones.

**Zinc Ethid—Zinc ethyl**—$(C_2H_5)_2Zn$—is obtained by heating at 130° (266° F.), in a sealed tube, a mixture of zinc amalgam and ethyl iodid, and distilling the product without contact of air.

It is a colorless liquid, sp. gr. 1.182, boils at 118° (244.4° F.). On contact of air it ignites, burns with a flame bordered with green, and gives off dense clouds of zinc oxid. On contact with water it is decomposed into zinc hydroxid and ethane.

## NITROGEN DERIVATIVES OF THE PARAFFINS.

### NITROPARAFFINS.

The univalent group ($NO_2$) is designated by the syllable **nitro** in the names of compounds containing it.

The **mononitroparaffins**—isomeric with the nitrous esters (p. 311), are derived from the paraffins by the substitution of $NO_2$ for an atom of hydrogen, and are distinguished as *primary*, *secondary*, and *tertiary*, in the same manner as the corresponding alcohols (p. 240) according as the $NO_2$ is united to $CH_2$,CH, or C. They are formed by the action of the alkyl iodids upon silver nitrite: $CH_3I+AgNO_2=AgI+CH_3NO_2$.

They are not acted upon by caustic potash, which readily decomposes the isomeric nitrous esters: $NO_2.C_2H_5+KHO=KNO_2+C_2H_5.HO$.

Nascent hydrogen converts them first into hydroxylamin compounds (p. 105): $CH_3.NO_2+2H_2=CH_3.NH.OH+H_2O$, which are in turn further reduced to monamins, or amidoparaffins: $CH_3.NH.OH+H_2=NH_2.CH_3+H_2O$.

Nitrous acid converts the primary nitroparaffins into **nitrolic acids**, as **ethyl-nitrolic acid**, $CH_3.C\begin{smallmatrix}NO_2\\NOH\end{smallmatrix}$, the liquid assuming a red color. The same agent converts the secondary nitroparaffins into **pseudonitrols**, as **propyl pseudonitrol**, $\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix}\!\!>\!C\!<\!\begin{smallmatrix}NO_2\\NO\end{smallmatrix}$, the liquid becoming blue. Upon the tertiary nitroparaffins nitrous acid has no action. These reactions are utilized to distinguish primary, secondary, and tertiary alcohols from each other.

## AMINS AND AMMONIUM DERIVATIVES.

The amins are compounds derived from ammonia by the substitution of hydrocarbon (non-acid) radicals for a part or all of its hydrogen.

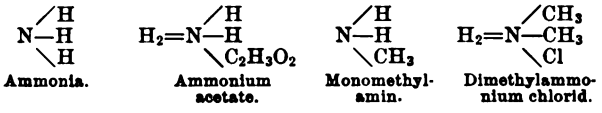
They are classified into **monamins**, derived from a single molecule of ammonia, **diamins**, derived from two such molecules, and **triamins**, derived from three.

## MONAMINS AND THEIR DERIVATIVES.

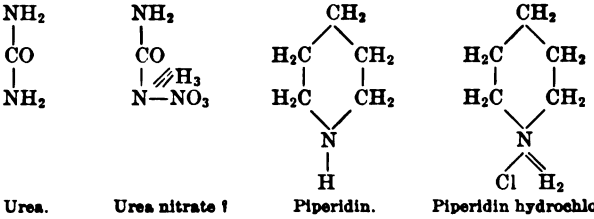
The monamins are **primary**, **secondary**, or **tertiary**, as one, two, or three of the hydrogen atoms of ammonia have been replaced. They are also distinguished as **amin**, **imin**, and **nitril bases**. When, in secondary or tertiary amins, the substituted radicals are alike the amins are designated as **simple**, when the radicals are different the amins are **mixed**. The primary monamins, containing the group $NH_2$, are **amido-paraffins**; while the secondary, containing the group NH, are **imido-paraffins**. The monamins have the algebraic formula, $NC_nH_{2n+3}$.

The monamins are sometimes called **compound ammonias**, from their resemblance to ammonia in their chemical properties, as well as from their origin. They combine with water to produce **quarternary ammonium hydroxids**, similar in constitution, alkalinity, and basicity to ammonium hydroxid; and with acids, without elimination of hydrogen, to form salts, similar to the ammoniacal salts.

The aliphatic monamins are the most simply constituted of a great variety of nitrogen derivatives, including the amids (p. 345), such as urea, and the vegetable alkaloids (p. 469), which have this in common with the amins, that they are basic in character, and, in combining with acids, form salts in the same manner as ammonia does, i. e., by change of the nitrogen valence from three to five, and, consequently, without elimimination of hydrogen; thus:



Ammonia. Ammonium acetate. Monomethyl-amin. Dimethylammo-nium chlorid.



Urea. Urea nitrate ? Piperidin. Piperidin hydrochlorid.

The naming of these compounds has been the subject of much discussion. As the substances formed by the union of ammonia with acids are regarded as salts of ammonium, not of ammonia, so these compounds are not salts of urea, piperidin, morphin, etc., but salts of hypothetical bases, containing a quinquivalent nitrogen atom, which in the free base is trivalent. The names: *ureium nitrate*, *piperidium chlorid*, *morphium sulfate*, etc., are therefore the analogues of *ammonium acetate* and *dimethylammonium chlorid*. For the chlorin, bromin, and iodin compounds the names: piperidin hydrochlorid, morphin hydrobromid, quinin hydroiodid, etc., may be conveniently retained, they being regarded as the free bases, plus hydrogen, plus the halogen.

The alkalinity and solubility in water of the primary monamins are greater than those of the secondary, and those of the secondary greater than those of the tertiary. Their chlorids form sparingly soluble compounds with platinic chlorid. The following formulæ indicate their constitution:

| $N{-}H_2(C_2H_5)$ | $N{-}H(CH_3)(C_2H_5)$ | $N(CH_3)_3$ | $(CH_3)_4N.OH$ | $(C_2H_5)_4N.Cl$ |
|---|---|---|---|---|
| Ethylamin. (Primary). | Methyl-ethylamin. (Secondary). | Trimethyl-amin. (Tertiary). | Tetramethyl ammonium hydroxid. | Tetrethyl ammonium chlorid. |

The **primary monamins** are formed: (1) by distilling the isocyanic esters with caustic potash: $CO:N.C_2H_5+2KHO=NH_2.C_2H_5+CO_3K_2$; (2) by heating the alkyl iodids, or the nitric esters, with alcoholic ammonia: $C_2H_5I+NH_3=NH_2.C_2H_5+HI$, or $C_2H_5.NO_3+NH_3=NH_2.C_2H_5+HNO_3$; (3) by the action of nascent H in alcoholic solution upon the nitrils (p. 340): $CH_3.CN+2H_2=NH_2.C_2H_5$; (4) by the action of nascent H upon the nitroparaffins: $CH_3.NO_2+3H_2=NH_2-CH_3+2H_2O$; (5) from the monamids (p. 345) of the fatty series monamins, containing one atom of carbon less than the amid, are formed by the action of bromin and potassium hydroxid. The reaction occurs in two stages. First a bromid is produced: $C_2H_5.CO.-NH_2+Br_2+KHO=C_2H_5.CO.NHBr+KBr+H_2O$, which is in turn converted into the amin with loss of the carbonyl group: $C_2H_5.CO.-NHBr+3KHO=C_2H_5.NH_2+CO_3K_2+H_2O+KBr$. (See also Ureids, p. 350.)

The **secondary monamins** are formed, as intermediate products, by the action of the alkyl iodids upon the primary monamins in the presence of excess of ammonia. The alkyl-ammonium iodid is first produced: $NH_2.C_2H_5+C_2H_5I=NH(C_2H_5)_2HI$, and this reacts with the ammonia: $NH(C_2H_5)_2HI+NH_3=NH(C_2H_5)_2+NH_4I$. The final products of the reaction are the tetrammonium iodids: $N(C_2H_5)_4I$.

**The tertiary amins** are obtained by the dry distillation of the quarternary ammonium hydroxids, iodids, or chlorids: $N(C_2H_5)_4I = N(C_2H_5)_3 + C_2H_5I$; or by heating the primary or secondary amins with excess of potassium-alkyl sulfate: $NH(CH_3)_2 + CH_3.K.SO_4 = N(CH_3)_3 + KHSO_4$.

The primary and secondary amins react with the esters to form alcohols and primary or secondary amids (p. 346). Thus methylamin and methyl acetate produce ethylic alcohol and acetamid: $NH_2CH_3 + CH_3.CO_2.CH_3 = CH_2OH.CH_3 + NH_2(CH_3.CO)$.

Nitrous acid eliminates the nitrogen from primary amins, with formation of alcohols, which may be primary, secondary or tertiary: $NH_2.C_2H_5 + HNO_2 = CH_2OH.CH_3 + N_2 + H_2O$. Nitrous acid converts the secondary amins into **nitroso-amins**, compounds in which an atom of hydrogen is replaced by (NO), the "nitroso" group: $NH(CH_3)_2 + HNO_2 = N(CH_3)_2.NO + H_2O$.

The primary monamins, when warmed with chloroform and alcoholic potash, yield **carbylamins, isocyanids, or isonitrils** (p. 340): $NH_2.C_2H_5 + CHCl_3 + 3KHO = CN.C_2H_5 + 3KCl + 3H_2O$. (See Chloroform, test 1, p. 235.)

When etheral solutions of primary monamins and of carbon disulfid are evaporated, a residue is obtained which, when heated in aqueous solution with $AgNO_3$, $Fe_2Cl_6$, or $HgCl_2$ forms a sulfid of the metal and a "mustard oil," having a pungent odor. This is Hoffman's test for primary monamins (see p. 344).

**Methylamin**—*Methylia*—$NH_2(CH_3)$—is a colorless, inflammable gas; having a fishy, ammoniacal odor. One volume of $H_2O$ dissolves 1,154 volumes at 12.5° (54.5° F.). The aqueous solution possesses the odor of the gas, and is highly caustic and alkaline. It neutralizes the acids with formation of **methylammonium salts** (e. g., $NH_3(CH_3).NO_3$=methylammonium nitrate), which are for the most part crystallizable and very soluble in $H_2O$. Its chloraurate crystallizes in beautiful golden-yellow needles, soluble in water, alcohol, and ether. Its chloroplatinate crystallizes in golden-yellow scales, soluble in water, insoluble in alcohol.

See Trimethylamin, below.

**Dimethylamin**—*Dimethylia*—$NH(CH_3)_2$—is a liquid below 7.2° (45° F.); has an ammoniacal odor, and is quite soluble in $H_2O$. It constitutes about 50 per cent. of the commercial trimethylamin, which also contains 5 to 10 per cent. of trimethylamin, the remainder being a mixture of monomethylamin, isobutylamin, and propylamin. Its chloroplatinate forms long needles.

See Trimethylamin, below.

**Trimethylamin**—*Trimethylia*—$N(CH_3)_3$—59—is formed by the action of methyl iodid upon $NH_3$, and as a product of decomposition

of many organic substances, it being one of the products of the action of potash on many vegetable substances, alkaloids, etc. It also occurs naturally in cod liver oil, ergot, chenopodium, yeast, guano, human urine, the blood of the calf, and many flowers.

It is an oily liquid, having a disagreeable odor of fish; boils at 3.5° (38.3° F.); alkaline; soluble in $H_2O$, alcohol, and ether; inflammable. It combines with acids to form salts of trimethyl-ammonium, which are crystallizable. Its chloroplatinate crystallizes in octahedra, insoluble in alcohol.

Trimethylamin has long been known to exist in the pickle in which herrings have been preserved. More recently it has been found to be a product of putrefactive changes in fish, starch-paste, brain-tissue, muscular tissue, and other protein substances, being accompanied by lesser quantities of monomethylamin, dimethylamin, ethylamin, and diethylamin, as well as by other peculiar alkaloidal bodies. It has also been observed accompanying more active alkaloids in blood-serum, etc., which have served for the culture of various bacilli.

The commercial trimethlamin, obtained by the dry distillation of distillery waste, contains 5 to 10 per cent. of the substance whose name it bears. (See Dimethylamin, above.) It has frequently been mistaken by writers upon materia medica for its isomere *propylamin*, $\left.\begin{matrix}(C_3H_7)\\H_2\end{matrix}\right\}N$. which differs from it in odor, and in boiling at 50° (122° F.). Its chlorid, under the names **chlorid of propylamia, of secalia, of secalin,** has been used in the treatment of gout and rheumatism.

**Tetramethyl Ammonium Hydroxid**—$N(CH_3)_4OH$.—This substance, whose constitution is similar to that of ammonium hydroxid, is obtained by decomposing the corresponding iodid $(CH_3)_4NI$, formed by the action of methyl iodid upon trimethylamin. It is a crystalline solid; deliquescent; very soluble in $H_2O$; caustic; not volatile without decomposition. It attracts carbon dioxid from the air, and combines with acids to form crystallizable salts.

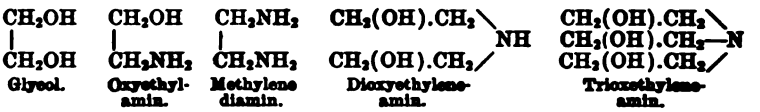
The iodid is said to exert an action upon the economy similar to that of curare.

**Tetraethylium Hydroxid** — $N.(C_2H_5)_4OH$ — forms deliquescent needles, is strongly alkaline, and is used as a solvent for uric acid.

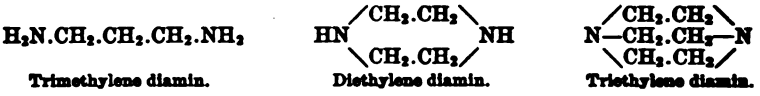
## OXYAMINS (HYDRAMINS), DIAMINS, IMINS AND DIIMINS.

The primary monamins may be considered as being derived from the monoatomic alcohols by the substitution of the amido group, $NH_2$, for the hydroxyl. From the dihydric alcohols, the glycols, two classes of amido compounds may be similarly derived. One of these, the

**oxyamins, or hydramins, contain a single amido group, and retain** an alcoholic hydroxyl. In the **diamins both hydroxyls are replaced** by amido groups. The oxyamins are primary, **secondary and tertiary** in the same manner as the monamins:




The diamins are primary, secondary, and tertiary, as they contain two groups $NH_2$, or two groups NH, or two N atoms ;



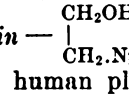

The primary diamins have the algebraic formula: $N_2C_nH_{2n+4}$; the secondary, $N_2C_nH_{2n+2}$; and the tertiary, $N_2C_nH_{2n}$.

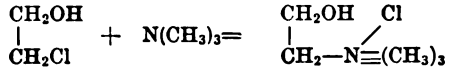
The secondary and tertiary diamins are cyclic compounds. (See Piperazin.)

The oxyamins are produced by the action of sulfuric acid and water upon the unsaturated amins (p. 377). Thus vinylamin yields oxyethylamin: $CH_2{:}CH.NH_2+H_2O=CH_2OH.CH_2NH_2$.

The diamins are obtained by reduction of the olefin dicyanids. Thus ethylene cyanid yields tetramethylene diamin: $CN.CH_2.CH_2.CN+4H_2=H_2N.CH_2.CH_2.CH_2.CH_2.NH_2$. Also, as hydrobromids, by heating the olefin bromids with alcoholic ammonia, to 100° (212° F.) under pressure : $Br.CH_2.CH_2.Br+2NH_3=H_3Br::N.CH_2.CH_2.N::H_3Br$.

The diamins form crystalline, insoluble compounds when shaken in alkaline solution with benzoyl chlorid, a property which they share with polyatomic alcohols and hexoses.

**Cholin** —*Trimethyloxethylammonium hydroxid*— *Bilineurin* — *Sincalin* —  —occurs in hops, in fungi, in certain seeds, in the human placenta, in bile and in the yolks of eggs. It is a constituent of the lecithins (p. 319). It is formed synthetically (as its chlorid) by the union of ethylene chlorhydrin and trimethylamin :




It is produced during the first twenty-four to forty-eight hours of putrefaction of animal tissues, from the decomposition of the lecithins, and diminishes from the third day, when other ptomaïns (neuridin, putrescin, cadaverin) increase in amount. When heated, it splits up into glycol and trimethylamin. Nitric acid converts it into muscarin.

It is a thick syrup, soluble in $H_2O$ and in alcohol, and strongly alkaline in reaction. Even in dilute aqueous solution it prevents the coagulation of albumin and redissolves coagulated albumin and fibrin. It is a strong base; attracts $CO_2$ from the air; forms with HCl a salt, soluble in alcohol, which crystallizes in plates and needles, resembling those of cholesterin. Its chloroplatinate is purified with difficulty; its chloraurate readily.

It is poisonous only in large doses, in which respect it differs from neurin (see below).

**Amanitin**—*Trimethyloxethylideneammonium hydroxid*—*Isocholin* —$\begin{matrix}CH_3 & OH\\ | & /\\ CHOH.N\equiv & (CH_3)_3\end{matrix}$— is an isomere of cholin, existing along with muscarin (see below) in *Agaricus muscarius*. It is produced by methylation of aldehydeammonia: $CH_3.CHOH.NH_2$. By oxidation with $HNO_3$ it yields muscarin.

**Muscarin**— $\begin{matrix}CH_2OH & OH\\ | & /\\ CHOH.N\equiv & (CH_3)_3\end{matrix}$ — is related to cholin, neurin and amanitin, from which it may be obtained by oxidation.

It occurs in nature in *Agaricus muscarius*, and is produced during putrefactive decomposition of proteins.

The free base occurs in very deliquescent, irregular crystals, or, if not perfectly dry, a colorless, odorless, and tasteless, but strongly alkaline syrup; readily soluble in all proportions in water and in alcohol; very sparingly soluble in chloroform; insoluble in ether. It is a more powerful base than ammonium hydroxid. When decomposed it yields trimethylamin. Its chloroplatinate crystallizes in octahedra. Its chlorid forms colorless, brilliant, deliquescent needles.

When administered to animals, muscarin causes increased secretion of saliva and tears; vomiting; evacuation of fæces, at first solid, later liquid; contraction of the pupils, almost to the extent of closure; diminution of the rapidity of the pulse; interference with respiration and locomotion; gradual sinking of the heart's action and respiration; and death. Atropin prevents the action of muscarin and diminishes its intensity when already established.

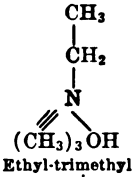
**Neurin**—*Trimethylvinylammonium hydroxid*— $\begin{matrix}CH_2 & OH\\ \| & /\\ CH.N\equiv & (CH_3)_3\end{matrix}$ —is a base resembling cholin, for which reason it is considered here, although its proper place is as a derivative of vinylamin (q. v.). It has been obtained from brain tissue and from the suprarenal capsule, probably as a product of decomposition of protagon. It is produced from cholin by boiling with baryta water. The same body is one of the alkaloids produced by the putrefaction of muscular tissue, and is endowed with poisonous qualities, resembling, but less intense than, those of muscarin.

**Betaïns**—are anhydrids having the general formula: $\begin{matrix}COO\\ |\ \diagdown\\ R''—N\equiv\end{matrix}$, corresponding to substances of mixed function, partly acid and partly quarternary ammonium: $\begin{matrix}COOH\ \ OH\\ |\ \ \diagup\\ R''—N\equiv\end{matrix}$, in which R'' may be any bivalent hydrocarbon radical, and in which the three remaining nitrogen valences may be satisfied by univalent radicals or by a trivalent radical. Or the arrangement of the valences may be reversed, as in nicotic-methyl betaïn: $\begin{matrix}COO———\\ |\ \ \ \ \ \ |\\ (C_5H_4)'''\equiv N—CH_3.\end{matrix}$

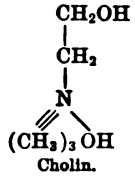
**Betaïn**—*Trimethyl-acetic betaïn—Oxyneurin—Oxycholin—Lycin—Trimethyl-glycocoll*—$\begin{matrix}COO\\ |\ \diagdown\\ CH_2—N\equiv(CH_3)_3\end{matrix}$—was first obtained from beet-juice (*Beta vulgaris*). It exists in beet-sugar molasses, in cotton-seed, and in malt. It is formed by several synthetic methods, e. g., by the action of methyl iodid upon amido-acetic acid (p. 363): $\begin{matrix}COOH\\ |\\ CH_2.NH_2\end{matrix}+3CH_3I=3HI+\begin{matrix}COO\\ |\ \diagdown\\ CH_2—N\equiv(CH_3)_3.\end{matrix}$; or by the interaction of monochloracetic acid and trimethylamin: $\begin{matrix}COOH\\ |\\ CH_2Cl\end{matrix}+N(CH_3)_3=\begin{matrix}COO\\ |\ \diagdown\\ CH_2—N\equiv(CH_3)_3\end{matrix}+HCl.$

Betaïn crystallizes in large, deliquescent crystals, with one molecule of water of crystallization, very soluble in water and in alcohol. It is decomposed by heat with evolution of trimethylamin, a fact which is utilized to obtain that substance from beet-molasses. It is strongly basic and forms crystalline salts. Its chloraurate is crystalline and very sparingly soluble in cold water.

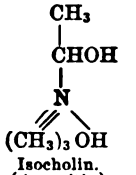
The relations of the oxyamin bases are shown in the following formulæ:



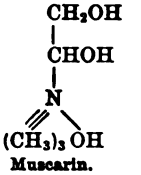
Ethyl-trimethyl ammonium hydroxid



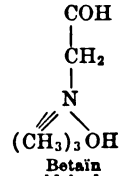
Cholin.



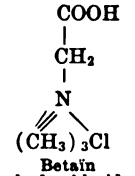
Isocholin. (Amanitin).



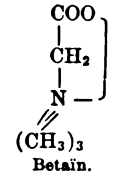
Muscarin.



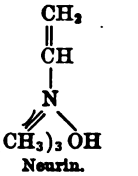
Betaïn aldehyde.



Betaïn hydrochlorid.



Betaïn.



Neurin.

Among the diamins are included several of the alkaloidal products of putrefaction known as **ptomaïns.**

**Ethylenediamin**—$H_2N.(CH_2)_2.NH_2$—is a strongly alkaline liquid, boiling at 116.5° (241.7° F.). With acetyl chlorid it forms **diacetyl-ethylene diamin,** $\begin{matrix}CH_2.NH.CO.CH_3\\ |\\ CH_2.NH.CO.CH_3\end{matrix}$, which is decomposed by heat with formation of a cyclic amidin base (p. 334), **ethylene-ethenyl amidin, or lysidin,** $\begin{matrix}CH_2.NH\\ |\\ CH_2.N\end{matrix}\!\!>\!\!C.CH_3$, a crystalline solid, fusing at 105° (221° F.), which is also prepared by heating ethylenediammonium chlorid with sodium acetate, and has been used as a solvent for uric acid.

**Trimethylenediamin**—$H_2N.(CH_2)_3.NH_2$—is said to have been obtained from the cultures of the comma bacillus. It has been obtained synthetically by the second method given on p. 330. It is an alkaline liquid, boiling at 135° (275° F.).

**Tetramethylenediamin—Putrescin**—$H_2N.(CH_2)_4.NH_2$—is produced, along with the cadaverin, during the putrefaction of muscular tissue, internal organs of man and animals, and of fish, and in the culture media of the comma bacillus from three days to four months. The free base is a colorless liquid (solid below 27°) having a seminal odor, which absorbs $CO_2$ from the air and unites with acids to form crystalline salts. It is not actively poisonous.

**Pentamethylenediamin—Cadaverin**—$H_2N.(CH_2)_5.NH_2$—is isomeric with neuridin and is produced during the later stages of putrefaction of many animal tissues, the cholin disappearing as this and the other diamins are formed. The free base is a clear syrupy liquid, having a strong disagreeable odor, resembling that of coniïn, boils at 175°, and fumes in air. It absorbs $CO_2$ rapidly, with formation of a crystalline carbonate. Its salts are crystalline. The chlorid on dry distillation is decomposed into ammonium chlorid and piperidin (p. 461).

**Hexamethylenediamin**—$H_2N.(CH_2)_6.NH_2$—is formed during putrefaction of muscular tissue and pancreas. It is a crystalline solid, fusing at 40° (104° F.) and boiling at 195° (383° F.).

**Neuridin**—$C_5H_{14}N_2$—a diamin of undetermined constitution, isomeric with cadaverin, is produced, along with cholin (p. 330), during the earlier stages of putrefaction, particularly of gelatinoid substances, and increases in quantity as putrefaction advances, while the quantity of cholin diminishes. The free base is a gelatinous substance, having a very marked seminal odor, readily soluble in water, insoluble in alcohol and in ether. Its chlorid is crystalline and very soluble in water. It seems to be non-poisonous when pure.

**Saprin**—$C_4H_{16}N_2$—another diamin of undetermined constitution.

has been obtained from putrid spleens and livers after three weeks' putrefaction.

**Mydalein** is still another putrid product of undetermined composition, but probably a diamin containing four or five carbon atoms, which forms a difficultly crystallizable, hygroscopic chlorid, which is actively poisonous. Five milligrams administered hypodermically to a cat causes death after profuse diarrhœa and secretion of saliva, violent convulsions and paralysis, beginning with the extremities and extending to the muscles of respiration.

**Spermin**—$C_2H_5N$—probably ethylene-imin, $\begin{matrix}CH_2\\|\\CH_2\end{matrix}\!\!>\!NH$, has been obtained from semen, testicles, ovaries, prostate, thyroid, pancreas, and spleen. Its phosphate forms crystals, known as Leyden, Böttcher's, or Charcot's crystals, which are met with in anatomical preparations preserved in alcohol, in dried semen, in sputa and nasal secretions, in the blood, spleen, and other organs of leucocythæmics and anæmics, and in fæces. A substance, probably identical with spermin, is also found in the cultures of the comma bacillus on beef-broth. The free base forms crystals, which rapidly absorb carbon dioxid from air, are readily soluble in water and in alcohol, insoluble in ether, and strongly alkaline in reaction. The Charcot crystals are insoluble in alcohol, ether and chloroform, difficultly soluble in water, easily soluble in dilute acids or alkalies.

The **imins**, also called imids (but see p. 347), are formed by the substitution of bivalent hydrocarbon groups for two hydrogen atoms in a single molecule of ammonia; the **diimins**, also called diamids, by the substitution of two such groups for four hydrogen atoms in two molecules of ammonia. These compounds are cyclic, and include some important members of the aromatic series.

When the diammonium chlorids are heated ammonium chlorid is split off, and an imin or a diimin is formed. Thus **piperidin** (p. 461) is produced from pentamethylene diamin; and **piperazin** (p. 462) from ethylene diamin:

$$ClH_3\overset{\blacktriangledown}{N}.CH_2.CH_2.CH_2.CH_2.CH_2.\overset{\blacktriangledown}{N}H_3Cl = NH_4Cl + ClH_2\overset{\blacktriangledown}{N}\begin{matrix}CH_2.CH_2\\CH_2.CH_2\end{matrix}\!\!>\!CH_2$$

$$2ClH_3\overset{\blacktriangledown}{N}.CH_2.CH_2.\overset{\blacktriangledown}{N}H_3Cl = 2NH_4Cl + ClH_2\overset{\blacktriangledown}{N}\begin{matrix}CH_2.CH_2\\CH_2.CH_2\end{matrix}\!\!>\!\overset{\blacktriangledown}{N}H_2Cl$$

## AMIDINS—AMIDOXIMS—HYDROXAMIC ACIDS.

The **amidins** contain both the amido group, $NH_2$, and the imido group, NH, and have the general formula: $R.C\begin{matrix}NH_2\\\diagdown NH\end{matrix}$, in which R is any univalent hydrocarbon radical.

They are formed by heating the nitrils (p. 340) with ammonium chlorid. Thus acetonitril yields **acetamidin**: $CH_3.C:N+NH_4Cl=HCl+CH_3.C\langle^{NH_2}_{NH}$. They are also formed by action of HCl upon the amids. Indeed, they may be considered as being derived from the amids (p. 345) by substitution of NH for the carbonyl oxygen: $CH_3.C\langle^{NH_2}_{O}$, acetamid: $CH_3.C\langle^{NH_2}_{NH}$, acetamidin. The amidins are monacid bases, very unstable when free.

The **amidoxims** are derived from the amidins by substitution of OH for hydrogen, e. g., $CH_3.C\langle^{NH_2}_{N.OH}$, **ethenylamidoxim.** They are very unstable compounds, formed by the action of hydroxylamin upon nitrils or upon amidins (p. 360).

**Hydroxamic acids** contain the **oxim** group, N.OH, while the amido group of the amidin is replaced by hydroxyl: $CH_3.C\langle^{OH}_{N.OH}$, **acetohydroxamic** acid.

## GUANIDIN AND ITS DERIVATIVES.

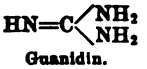
**Guanidin—Carbotriamin**—$CH_5N_3$—was first obtained by oxidation of guanin (p. 357). Its synthesis has been accomplished by heating together ethyl orthocarbonate, $C(OC_2H_5)_4$, and $NH_3$. It is a crystalline substance, which absorbs $CO_2$ and $H_2O$ from the air, and forms crystalline salts. Some of its derivatives are important physiologically.

Guanidin, containing the group $.C\langle^{NH_2}_{NH}$, is an amidin. It may also be considered as a triamin, derived from three ammonia molecules, $H_2N—C\langle^{NH_2}_{NH}$. It is related to amidocarbonic acid, to urea and to pseudourea, as is indicated by the formulæ:

| $NH=C\langle^{NH_2}_{NH_2}$ | $O=C\langle^{NH_2}_{NH_2}$ | $NH=C\langle^{NH_2}_{OH}$ | $O=C\langle^{NH_2}_{OH}$ |
|---|---|---|---|
| Guanidin. | Urea. | Pseudourea. | Amido carbonic acid. |

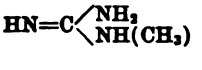
**Methyl-guanidin—Methyluramin**—$HN:C(NH_2)NH(CH_3)$—was first obtained by the oxidation of creatin and of creatinin (see below). It has also been obtained as a product of putrefaction of muscular tissue at a low temperature in closed vessels, when it probably results from the decomposition of creatin. It is a colorless, crystalline, deliquescent, strongly alkaline substance, and is highly poisonous.

The relation of guanidin and methyl-guanidin to each other and to creatin and creatinin is shown by the following formulæ:

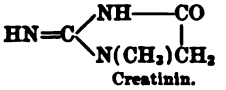


Guanidin.

Creatin.



Methyl-guanidin.



Creatinin.

**Creatin**—*Methyl-guanidin acetic acid*—$C_4H_9N_3O_2+Aq$—is, as is shown by the above graphic formula, a complex amido-acid (p. 361). It is a normal constituent of the juices of muscular tissue, brain, blood, and amniotic fluid. It is formed synthetically by the union of methyl glycocoll (p. 363), and cyanamid (p. 344): $CH_2(NH.CH_3).COOH+NC.NH_2=HN=C\begin{matrix}NH_2\\N(CH_3).CH_2.COOH\end{matrix}$.

It is best obtained from the flesh of the fowl, which contains 0.32 per cent., or from beef-heart, which contains 0.14 per cent. It is soluble in boiling $H_2O$ and in alcohol, insoluble in ether; crystallizes in brilliant, oblique, rhombic prisms; neutral; tasteless; loses Aq at 100° (212° F.); fuses and decomposes at higher temperatures. When long heated with $H_2O$, or treated with concentrated acids, it loses $H_2O$, and is converted into creatinin. Baryta water decomposes it into sarcosin and urea. It is not precipitated by silver nitrate, except when it is in excess and in presence of a small quantity of potassium hydroxid. The white precipitate so obtained is soluble in excess of potash, from which a jelly separates, which turns black, slowly at ordinary temperatures, rapidly at 100° (212° F.). A white precipitate, which turns black when heated, it also formed when a solution of creatin is similarly treated with mercuric chlorid and potash.

**Creatinin**—*Methyl guanidin acetic lactam*—$C_4H_7N_3O$—113—a product of the dehydration of creatin, is a normal and constant constituent of the urine and amniotic fluid, and also exists in the blood and muscular tissue.

It crystallizes in oblique, rhombic prisms, soluble in $H_2O$ and in hot alcohol, insoluble in ether. It is a strong base, has an alkaline taste and reaction; expels $NH_3$ from the ammoniacal salts, and forms well-defined salts, among which is the double chlorid of zinc and creatinin $(C_4H_7N_3O)_2ZnCl_2$, obtained in very sparingly soluble, oblique prismatic crystals, when alcoholic solutions of creatinin and zinc chlorid are mixed.

**Lysatin**—$C_6H_{13}N_3O_2$, or **Lysatinin**—$C_6H_{11}N_3O+H_2O$—one of the **hexon bases**, formed in the decomposition of protein bodies, is a superior homologue of creatin or of creatinin.

**Cruso-creatinin**—$C_5H_8N_4O$—is an orange-yellow, crystalline solid, alkaline in reaction; **Xantho-creatinin**—$C_5H_{10}N_4O$—is in yellow crys-

talline plates; **Amphi-creatinin**—$C_9H_{19}N_7O_4$—forms yellowish-white prismatic crystals. These are basic substances, forming crystalline chlorids, and belonging to the class of **leucomaïns**, which include alkaloidal substances produced by physiological processes. (See p. 496). They are obtained from the juices of muscular tissue, and from Liebig's meat extract, in which they accompany creatin and creatinin.

### HYDRAZINS.

The **hydrazins** are derivatives of the hypothetical diamidogen, $H_2N.NH_2$ (p. 105), by substitution of aliphatic or aromatic radicals, alcoholic, phenolic or acid, for one or more of the hydrogen atoms in the same way as the amins are derived from ammonia. There are, therefore, primary, secondary, tertiary and quarternary hydrazins; and they may be **symmetrical**, as $C_2H_5.HN.NH.C_2H_5$ and $C_6H_5.HN.NH.C_2H_5$, or **unsymmetrical**, as $C_6H_5.HN.NH_2$ and $(C_2H_5)_2N.NH_2$. The aliphatic hydrazins are obtained from the alkyl-ureas, by conversion into nitroso-amins, and reduction. Most of the hydrazins, some of which are of considerable interest, are derivatives of phenyl-hydrazin, $C_6H_5.HN.NH_2$, and, containing a cyclic chain $C_6H_5$, will be considered among the aromatic compounds.

### NITRILS — AZOPARAFFINS — CYANOGEN COMPOUNDS.

These substances may be considered either as compounds of the univalent radical **cyanogen** $(C^{iv}\,N''')'$; or as paraffins, $C_nH_{2n+2}$, in which three atoms of hydrogen have been replaced by the trivalent $N'''$ atom, hence **azoparaffins**; or as **nitrils**, compounds of N with the trivalent radicals $C_nH_{2n-1}$.

**Hydrogen Cyanid**—*Formonitril*—*Cyanogen hydrid*—**Hydrocyanic acid**—**Prussic acid**—$HC\vdots N$—exists ready formed in the juice of *cassava*, and is formed by the action of $H_2O$ upon bitter almonds, cherry-laurel leaves, and other vegetable products containing **amygdalin**, a glucosid, which is decomposed into glucose, benzoic aldehyde (p. 410), and hydrocyanic acid, when warmed with water. It is also formed in a great number of reactions: by the passage of the electric discharge through a mixture of acetylene and nitrogen: $HC\vdots CH + N_2 = 2HC\vdots N$; by the action of chloroform on ammonia: $NH_3 + CHCl_3 = 3HCl + HCN$; by the distillation of, or the action of $HNO_3$ upon, many organic substances; by the decomposition of cyanids (see Nitrils, below).

It is always prepared by the decomposition of a cyanid or a ferrocyanid, usually by acting upon potassium ferrocyanid with

dilute sulfuric acid, and distilling. Its preparation in the pure form is an operation attended with the most serious danger, and should only be attempted by those well trained in chemical manipulation. For medical uses a very dilute acid is required; the acid. hydrocyanicum dil. (U. S. Br.) contains, if freshly and properly prepared, two per cent. of anhydrous acid. That of the French Codex is much stronger — ten per cent.

The pure acid is a colorless, mobile liquid, has a penetrating and characteristic odor; sp. gr. 0.7058 at 7° (44.6° F.); crystallizes at —15° (5° F.); boils at 26.5° (79.7° F.); is rapidly decomposed by exposure to light. The dilute acid of the U. S. P. is a colorless liquid, having the odor of the acid; faintly acid, the reddened litmus returning to blue on exposure to air; sp. gr. 0.997; 10 grams of the acid should react without excess with 1.27 gram of silver nitrate. The dilute acid deteriorates on exposure to light, although more slowly than the concentrated; a trace of phosphoric acid added to the solution retards the decomposition.

Most strong acids decompose HCN. The alkalies enter into double decomposition with it to form cyanids. It is decomposed by Cl and Br, with formation of cyanogen chlorid or bromid. Nascent H converts it into methylamin.

**Analytical Characters.**—(1) With silver nitrate: a dense, white ppt.; which is not dissolved on addition of $HNO_3$ to the liquid, but dissolves when separated and heated with concentrated $HNO_3$; soluble in solutions of alkaline cyanids or thiosulfates. (2) Treated with $NH_4HS$, evaporated to dryness, and ferric chlorid added to the residue: a blood-red color, which is discharged by mercuric chlorid. (3) With potash and then a mixture of ferrous and ferric sulfates: a greenish ppt., which is partly dissolved by HCl, leaving a pure dark-blue precipitate. (4) Heated with a dilute solution of picric acid and then cooled: a deep-red color. (5) Moisten a piece of filter-paper with a freshly prepared alcoholic solution of guaiac; dip the paper into a very dilute solution of $CuSO_4$, and, after drying, into the liquid to be tested. In the presence of HCN it assumes a deep-blue color. (6) Add a few drops of potassium nitrite solution, then two or three drops of ferric chlorid solution, and enough dilute $H_2SO_4$ to turn the color to yellow. Heat just to boiling; cool, add a few drops of $NH_4HO$, filter, and add to the filtrate a few drops of dilute, colorless ammonium sulfhydrate: a violet color, changing to blue, then to green and yellow (p. 345).

**Toxicology.** — Hydrocyanic acid is a violent poison, whether it be inhaled as vapor, or swallowed, either in the form of dilute acid, of soluble cyanid, or of the pharmaceutical preparations containing it, such as oil of bitter almonds and cherry-laurel water; its action being

more rapid when taken by inhalation or in aqueous solution than in other forms. When the medicinal acid is taken in poisonous dose, its lethal effect may seem to be produced instantaneously; nevertheless, several respiratory efforts usually are made after the victim seems to be dead, and instances are not wanting in which there was time for considerable voluntary motion between the time of ingestion of the poison and unconsciousness. In the great majority of cases the patient is either dead or fully under the influence of the poison on the arrival of the physician, who should, however, not neglect to apply the proper remedies if the faintest spark of life remain. Chemical antidotes are, owing to the rapidity of action of the poison, of no avail, although possibly chlorin, recommended as an antidote by many, may have a chemical action on that portion of the acid already absorbed. The treatment indicated is directed to the maintenance of respiration; cold douche, galvanism, artificial respiration, until elimination has removed the poison. If the patient survive an hour after taking the poison, the prognosis becomes very favorable; in the first stages it is exceedingly unfavorable, unless the quantity taken has been very small.

In cases of death from hydrocyanic acid the odor of the poison may be observed in the apartment, or upon opening the body. In cases of suicide or accident, the vessel from which the poison has been taken will usually be found in close proximity to the body, although the absence of such vessel is not proof that the case is necessarily one of homicide.

Notwithstanding the volatility and instability of the poison, its presence has been detected two months after death, although the chances of separating it are certainly the better the sooner after death the analysis is made. The search for hydrocyanic acid is combined with that of phosphorus; the part of the distillate containing the more volatile products is examined by the tests given above. It is best, when the presence of free hydrocyanic acid is suspected, to distil at first without acidulating. In cases of suspected homicide by hydrocyanic acid, the stomach should never be opened until immediately before the analysis.

**Cyanogen Chlorids.**—Two polymeric chlorids are known: **Cyanogen chlorid**, CNCl, formed by the action of Cl upon anhydrous HCN or upon $Hg(CN)_2$ in the dark. It is a colorless gas, condensing to a liquid at 15° (59° F.); intensely irritating and poisonous. **Tricyanogen chlorid**, $C_3N_3Cl_3$, is formed, as a crystalline solid, when anhydrous HCN is acted upon by Cl in sunlight. It fuses at 146° (294.8° F.).

**Cyanids.**—The most important of the simple metallic cyanids are those of K and Ag (pp. 181, 184, also p. 344).

**Nitrils.**—The hydrocyanic esters of the univalent alcoholic radicals are called **acid nitrils**, because of their formation from the amids (p. 345), by the reaction given under (3) below. Hydrocyanic acid, being produced from formamid, is **formonitril**; methyl cyanid, derived from acetamid, is **acetonitril**, etc. They are also derivable from the ammonium salt of the acid by elimination of the elements of two molecules of water. Their formulæ may be derived from those of the acids by substitution of N for the trivalent OOH of the carboxyl.

The nitrils are produced: (1) By heating the haloid esters (p. 233) with alcoholic solution of potassium cyanid at 100°: $CH_3.CH_2I+KCN=CH_3.CH_2.CN+KI$. (2) By distilling a mixture of potassium cyanid and the potassium salt of a monoalkyl sulfate. Thus, ethyl cyanid is produced from potassium ethylsulfate: $KCN+SO_4.C_2H_5.K=K_2SO_4+C_2H_5.CN$. (3) By complete dehydration, by the action of $P_2O_5$, of the ammoniacal salt of the acid, or of its amid (p. 346). Thus acetonitril is obtained from ammonium acetate: $CH_3.COO(NH_4)=CH_3.CN+2H_2O$; or from acetamid: $CH_3.CO.NH_2=CH_3.CN+H_2O$. (4) By the action of acidyl chlorids upon silver cyanate. Thus, with acetyl chlorid, methyl cyanid is formed: $CNOAg+CH_3.CO.Cl=AgCl+CO_2+CH_3.CN$.

The nitrils combine with nascent hydrogen to form primary amins. Thus acetonitril forms ethylamin: $CH_3.CN+2H_2=C_2H_5.NH_2$. Hydrating agents convert them into the ammonium salts of the corresponding acids. Thus ammonium propionate is derived from ethyl cyanid: $C_2H_5.CN+2H_2O=C_2H_5.COO(NH_4)$. Or, when acted upon by concentrated sulfuric acid, hydrogen peroxid, or concentrated hydrochloric acid, they take up one molecule of water and form amids (p. 346). Thus acetonitril forms acetamid: $CH_3.CN+H_2O=CH_3.CO.NH_2$.

**Methyl Cyanid**—**Acetonitril**—$CH_3.CN$—is a colorless liquid, b. p. 81.6°, having an agreeable odor, sparingly soluble in water, obtained by distilling ammonium acetate or acetamid with $P_2O_5$.

The **isocyanids, carbylamins, or carbamins** are isomeres of the nitrils, which differ from the latter in constitution in that, in the nitrils, the nitrogen is trivalent, and the alkyl group is in union with carbon, e. g., methyl cyanid, $N\equiv C—CH_3$, while in the carbylamins the nitrogen is quinquevalent, and the alkyl is in union with nitrogen, e. g., methyl isocyanid, $C\equiv N—CH_3$. The isocyanids, when acted upon by hydrating agents, do not yield ammonium salts of the corresponding acids, as do the nitrils (see above), but are decomposed into formic acid and a primary amin. Thus ethyl isocyanid does not yield propionic acid, but formic acid and ethylamin: $NC.C_2H_5+2H_2O=H.COOH+C_2H_5.NH_2$.

The isocyanids are formed: (1) by the action of a primary monamin on chloroform in the presence of caustic potash. Thus methyl isocyanid is derived from methylamin: $CH_3.NH_2+CHCl_3=3HCl+NC.CH_3$. (pp. 235, 328); (2) by the action of alkyl iodids upon silver cyanid: $CH_3I+AgCN=AgI+NC.CH_3$.

**Methyl Isocyanid**—*Methyl carbylamin*—*Isoacetonitril*—$CH_3.NC$—is a colorless liquid, b. p., 58°, having a disagreeable odor, and giving off highly poisonous vapor. It is formed by the reactions given above, and is said to exist in the venom of toads.

**Phenyl Isocyanid**—*Isobenzonitril*—$C_6H_5.NC$—is a colorless liquid, not boiling without decomposition, having an intensely disagreeable odor, whose formation is utilized in a test for chloroform (p. 235).

Both nitrils and isonitrils combine with the hydracids to form crystalline salts, decomposable by water; the latter much more energetically than the former. They are all volatile liquids; the nitrils having ethereal odors when pure, the isonitrils odors which are very powerful and disagreeable.

**Nitrils of the Oxyacids.**—The nitrils of the α-acids of the oxyacetic series (p. 290) are also called **cyanhydrins, or oxycyanids,** and bear the same relation to the acids, as exists between the acids of the acetic series and their nitrils:

| | |
|---|---|
| $CH_3.COOH$ | $CH_3.CN$ |
| Acetic acid. | Acetonitril. |
| $CH_3.CHOH.COOH$ | $CH_3.CHOH.CN$ |
| α-lactic acid. | Lactic nitril. |

They are formed as additive products between hydrocyanic acid and the aldehydes and ketones: $HCN+CH_3.CHO=CH_3.CHOH.CN$, and $HCN+CH_3.CO.CH_3=\frac{CH_3}{CH_3}\!>\!C\!<\!\frac{CN}{OH.}$ By hydration they yield the corresponding acid and ammonia: $CH_3.CHOH.CN+2H_2O=CH_3.CHOH.COOH+NH_3$. These reactions are utilized in the synthesis of the oxyacids (p. 290).

**Nitrils of the Ketone Acids.**—These are the cyanids of the acidyls, as the nitrils are the cyanids of the alkyls, and are formed by heating the acidyl chlorids with silver cyanid. Thus **acetyl cyanid** is produced from acetyl chlorid: $CH_3.CO.Cl+AgCN=CH_3.CO.CN+AgCl$; or by dehydration of the aldoxims (p. 360) of the α-aldehyde ketones. Thus oximido-acetone yields acetyl cyanid: $CH_3.CO.CH:N.OH=CH_3.CO.CN+H_2O$. They are unstable, and are decomposed by water into hydrocyanic acid and their corresponding acids: $CH_3.CO.CN+H_2O=CH_3.COOH+CNH$.

**Nitrils of Dicarboxylic Acids.**—Two nitrils are derivable from a dicarboxylic acid, one being a **nitrilic acid,** the other a **dinitril.** The

nitrilic acid of oxalic acid is only known in its esters; its dinitril is dicyanogen:

| | | | |
|---|---|---|---|
| COOH | $CO(NH_2)$ | $COO(C_2H_5)$ | CN |
| COOH | $CO(NH_2)$ | CN | CN |
| Oxalic acid. | Oxamid. | Oxalnitrilic ethyl ester. | Dicyanogen. |

**Dicyanogen**—CN.CN—is prepared by heating mercuric cyanid, and is also formed by passing an electric arc between carbon points in an atmosphere of nitrogen.

It is a colorless gas, has a pronounced odor of bitter almonds; sp. gr., 1.8064 A. It burns in air with a purple flame, giving off N and $CO_2$. It is quite soluble in water, but the solutions soon turn brown, and then contain ammonium oxalate and formate, urea, and hydrocyanic acid. The brown color is due to the formation of **azulmic acid**, $C_4H_5N_5O$.

**Succinonitril**—*Ethylene cyanid*—$CN.CH_2.CH_2.CN$—is the dinitril of succinic acid. It is an amorphous solid, soluble in water, alcohol, and chloroform. Fuses at 55° (131° F.).

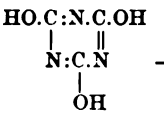
**Nitrils of Carbonic and Thiocarbonic Acids.**—These constitute the oxygen and sulfur compounds of cyanogen. Thus cyanic acid is the nitril of carbonic acid: $CO_3H(NH_4) = CONH + 2H_2O$, and thiocyanic acid that of thiocarbonic acid: $CO_2SH(NH_4) = CSNH + 2H_2O$.

Three structural formulæ of these compounds are possible: N≡C.-OH, O=C=N.H, and C≡N.OH. The first structure is that of the normal cyanic and thiocyanic acids, the second that of the isocyanates and isothiocyanates, the third that of fulminic acid.

**Cyanic Acid**—NC.OH—is obtained by distillation of cyanuric acid, or, in its salts, by calcining the cyanids in presence of an oxidizing agent, or by the action of dicyanogen upon solutions of the alkalies or alkaline carbonates.

It is a colorless liquid, only stable below 0° (32° F.); has a strong odor, resembling that of formic acid; and is soluble in water; gives off an irritating vapor; is vesicating to the skin; and is changed by exposure to air into its polymere, **cyamelid**, a white, porcelain-like solid.

**Cyanuric Acid**—*Tricyanic acid*—



—is produced by dry distillation of uric acid; by the action of heat or of Cl upon urea; by heating tricyanogen chlorid or bromid with water or with alkalies. It forms colorless crystals, odorless, almost tasteless, feebly acid, rather soluble in water. It is tribasic. It may be dissolved in strong

$H_2SO_4$ or $HNO_3$ without decomposition, but, when boiled with acids or alkalies, it is decomposed into carbon dioxid and ammonia; and, when distilled, into cyanic acid.

The ordinary potassium and ammonium cyanates are regarded as **isocyanates**, salts of **isocyanic acid**, or **carbimid**, O:C:NH. The ammonium salt, $O:C:N(NH_4)$, is converted into its isomere, urea, $H_2N.CO.NH_2$, by evaporation of its solution. The isocyanic esters serve for the generation of the alkyl ureas (p. 350).

**Fulminic Acid**—*Carbyloxim*—$C\equiv N.OH$—is a strongly acid substance, having the odor and poisonous qualities of hydrocyanic acid, whose Ag and Hg salts are formed by the action of nitrous acid upon alcohol and silver, or mercuric, nitrate. **Mercuric fulminate**, or **fulminating mercury**, crystallizes in white, soluble needles, and explodes violently upon shock. It is used in percussion caps, primers and cartridges. **Silver fulminate** is more violently explosive than the mercurial salt. **Fulminating gold** is not a fulminate, but **auroamidoimid**, $Au(NH)NH_2+3H_2O$.

**Fulminuric Acid**—$CN.CH(NO_2).C\langle^{OH}_{NH}$—metameric with cyanuric, and polymeric with cyanic and isocyanic acids, is a derivative of tartronic acid, COOH.CHOH.COOH; whose alkali salts are formed by boiling solutions of alkaline chlorids with mercuric fulminate.

**Thiocyanic Acid**—*Sulfocyanic acid*—*Cyanogen sulfhydrate*—$N\equiv C.SH$—is obtained by decomposition of its salts, which are formed by boiling solutions of the cyanids with sulfur; by the action of dicyanogen upon the metallic sulfids; and in several other ways.

The free acid is a colorless liquid, crystallizes at —12.5° (9.5° F.), acid in reaction. The prominent reaction of the acid and of its salts is the formation of a deep-red color with the ferric salts; the color being discharged by mercuric chlorid solution.

Thiocyanates exist in the human saliva and in the stomach-contents, in small amount. The free acid is poisonous.

**Isothiocyanic Esters**—*Mustard oils*—Isothiocyanic acid, S:C:NH, is not known in the free state. Its esters are called mustard oils, from the most important of the class, allyl isothiocyanate (p. 377), which is the essential oil of mustard.

The mustard oils are obtained: (1) by mixing ether solutions of primary amins and carbon disulfid, and evaporating the solutions, the amin salts of alkyl dithiocarbamic acids are formed (p. 350): $CS_2+2C_2H_5.NH_2=SC\langle^{NHC_2H_5}_{S(NH_3.C_2H_5)}$. On boiling aqueous solutions of these with $AgNO_3$, $Fe_2Cl_6$ or $HgCl_2$, the metallic sulfids are precipitated, and hydrogen sulfid and the mustard oils are formed, the latter distilling over. The reaction takes place in two stages:

$$SC\begin{matrix}NH.C_2H_5\\S(NH_2.C_2H_5)\end{matrix} + AgNO_3 = SC\begin{matrix}NH.C_2H_5\\SAg\end{matrix} + NO_3.N\begin{matrix}H_3\\C_2H_5\end{matrix}, \text{ and}$$

Ethylammonium ethylthiocarbamate. — Silver nitrate. — Silver ethyldithiocarbamate. — Ethylammonium nitrate.

$$2SC\begin{matrix}NH.C_2H_5\\SAg\end{matrix} = Ag_2S + H_2S + 2SC{:}N.C_2H_5$$

Ethyl isocyanate.

Hoffmann's test for the primary amins (p. 328) is based upon these reactions.

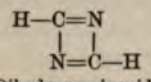
The mustard oils are liquids, insoluble in water, giving off vapors of penetrating odor and irritating to the eyes. When heated with water under pressure to 200° (392° F.), or with hydrochloric acid to 100° (212° F.), they are decomposed into carbon dioxid, hydrogen sulfid and amins: $SC{:}N.C_2H_5+2H_2O=CO_2+SH_2+NH_2.C_2H_5$. Heating with dilute $H_2SO_4$ decomposes them into amins and carbon oxysulfid, COS. With nascent hydrogen they yield thioformaldehyde and a primary amin: $SC{:}N.C_2H_5+2H_2=H.CSH+NH_2.C_2H_5$. Heated with monocarboxylic acids they form carbon oxysulfid, esters, and monamids (p. 345): $SC{:}N.C_2H_5+2CH_3.COOH=COS+CH_3.COO.C_2H_5+NH_2.CH_3.CO$. Their alcoholic solutions, when boiled with HgO, yield isocyanic esters, which are converted by water into the corresponding compound ureas.

Cyanamid—$CN.NH_2$—is the nitril of carbamic acid (p. 346): $OC{:}NH_2.O.NH_4-2H_2O=CN.NH_2$. It is formed by the action of cyanogen chlorid upon ammonia: $CNCl+2NH_3=NH_4Cl+CN.NH_2$. It forms colorless crystals, soluble in water, alcohol or ether. Corresponding to it are substituted cyanamids, which may be formed by using a primary amin in place of ammonia in the above-mentioned method of preparation: $CNCl+2NH_2.CH_3=NH_3.CH_3.Cl+CN.NHCH_3$.

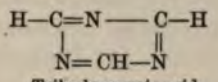
**Metallocyanids.**—The metallic compounds of cyanogen, the cyanids, may be divided into three classes: (1) the simple cyanids, such as potassium, silver, or mercuric cyanid, which resemble in constitution and general characters the chlorids, bromids and iodids; (2) the double cyanids, such as $AgK(CN)_2$, or $HgK_2(CN)_4$, which are constituted like other double salts. These salts have crystalline forms and solubilities of their own, independent of those of the simple cyanids of which they are made up. They are readily decomposed by cold acids, with liberation of hydrocyanic acid; (3) compound cyanids, or metallocyanids, in which the cyanogen groups are more intimately attached to the metal, in such manner that the ordinary analytical characters of the metals are completely masked; and when they are decomposed by cold acids hydrocyanic acid is not liberated, but a complex metallohydrocyanic acid, corresponding in constitution to the salt. The metals entering into the composition of the metal-

locyanids are iron (ferro- and ferricyanids), cobalt (cobalticyanids), and platinum (platinocyanids); also chromium and manganese in the *ic* form.

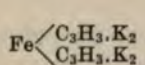
The metallocyanids are considered as derivatives of two hypothetical acids, polymeres of hydrocyanic acid: **dihydrocyanic acid** and **trihydrocyanic acid**, which, in the hydrometallocyanic acids and their salts are combined with the constituent metal, with loss of hydrogen, as shown in the following formulæ:



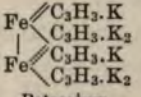
Dihydrocyanic acid.



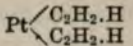
Trihydrocyanic acid.



Potassium ferrocyanid.



Potassium ferricyanid.



Hydroplatinocyanic acid.

**Hydronitroprussic Acid**—$Fe(CN)_5(NO)H_2$—contains the *nitroso* group NO, and is produced when potassium ferrocyanid is acted upon by nitric acid. Its sodium salt, **sodium nitroprussid**, is formed by neutralizing the acid with sodium carbonate. It forms brilliant red prisms; and is used as a test for sulfids, with which it forms a violet color. (See test No. 6, Hydrocyanic acid, p. 338.)

## AMIDS.

These compounds are similar in constitution to the amins (p.326), from which they differ in that the substituted radicals are acid in place of hydrocarbon radicals.

Like the amins they are classified into **monamids, diamids, triamids,** according as they are derived from one, two or three molecules of ammonia.

**Mixed amids** are also known, produced by the substitution of acid radicals for the remaining hydrogen of the primary and secondary amins, e. g., diethyl acetamid: $CH_3CO(C_2H_5)_2N$.

## MONAMIDS — AMIC ACIDS — IMIDS.

Like the monamins, the monamids are **primary, secondary,** or **tertiary,** as they contain one, two, or three substituted radicals.

The primary monamids corresponding to the monocarboxylic acids may also be considered as being derived from those acids by substitution of $NH_2$ for the OH of the group COOH. Thus acetamid, $CH_3.CO.NH_2$ is derived from acetic acid, $CH_3.CO.OH$.

The primary monamids are formed: (1) by the action of heat upon the ammonium salt of the acid, with elimination of the elements of one molecule of water: $CH_3.COO(NH_4)=H_2O+CH_3.CO.NH_2$. It will be remembered that the nitrils (p. 340) are derived from the ammoniacal salts by elimination of two molecules of water: $CH_3.COO(NH_4)=2H_2O+CH_3.CN$; (2) by addition of $H_2O$ to the nitrils. Thus hydrogen peroxid in alkaline solution converts acetonitril into acetamid: $2CH_3.CN+2H_2O_2=2CH_3.CO.NH_2+O_2$; (3) by the action of ammonia upon esters. Thus, ethyl acetate and ammonia produce acetamid and ethylic alcohol: $CH_3.COO(C_2H_5)+NH_3=CH_3.CO.NH_2+CH_3.CH_2OH$; (4) by the action of an acidyl chlorid upon dry ammonia. Thus, acetamid is produced by acetyl chlorid: $CH_3.CO.Cl+2NH_3=NH_4Cl+CH_3.CO.NH_2$.

The secondary monamids are obtained: (1) by the action of acidyl chlorids upon the primary monamids. Thus, diacetamid is produced from monacetamid: $CH_3.CO.NH_2+CH_3.CO.Cl=HCl+(CH_3CO)_2NH$; (2) by the action of hydrochloric acid upon the primary monamids at high temperatures; $2(CH_3.CO.NH_2)+HCl=NH_4Cl+(CH_3CO)_2NH$.

The tertiary amids of this series have been imperfectly studied. Some have been obtained by the action of acidyl chlorids upon metallic derivatives of secondary amids: $(CH_3.CO)_2NaN+CH_3.CO.Cl=(CH_3.CO)_3N+NaCl$; or by the union of anhydrids and nitrils at 200° (392° F.): $CH_3.CN+(CH_3.CO)_2O=(CH_3.CO)_3N$.

Monamids are also formed by the substitution of univalent remainders of dibasic acids for the hydrogen of a single molecule of ammonia. These amic acids are formed by carefully distilling the monoammonium salt of the acid. Thus, monoammonium oxalate yields oxamic acid: $COOH.COO(NH_4)=H_2O+COOH.CO.NH_2$.

Or they may be obtained from the imids as shown below.

Carbamic Acid—$OC\langle^{NH_2}_{OH}$—is not known in the free state. Its ammonium salt exists in commercial ammonium carbonate, and is produced by direct union of ammonia and carbon dioxid: $2NH_3+CO_2=OC\langle^{NH_2}_{O(NH_4)}$. It also exists normally in the urine, and is probably formed in the system as an intermediate product between the amido acids and urea. Indeed, carbamic acid is amido-formic acid (p. 362).

The esters of carbamic acid, called urethans, are more stable than its salts. They are formed by the action of ammonia upon the carbonic esters: $OC:(OC_2H_5)_2+NH_3=OC:NH_2.OC_2H_5+CH_3.CH_2OH$; also by the action of cyanogen chlorid on alcohols: $CNCl+2C_2H_5OH=OC:NH_2.OC_2H_5+C_2H_5Cl$.

Ethyl Urethan—$OC:NH_2.OC_2H_5$—is formed by the above reactions. It forms thin, large, transparent plates; fusible at 50° (122°

F.), boiling at 184° (363.1° F.), very soluble in alcohol and in water. It has been used as a hypnotic, either alone or combined with chloral in **uralium**, or **somnal**.

**Phenyl Urethan**—$OC:NH_2.OC_6H_5$—is a light white powder, almost insoluble in water, very soluble in alcohol, which is used as an antipyretic under the name **euphorine**.

Two atoms of hydrogen in a single molecule of ammonia may be replaced in a bivalent acid radical; in which case an **imid** is formed (p. 334). The imids are obtained by dehydration of the monoammonium salts or of the amic acids. Thus, monoammonium succinate, or succinamic acid yields **succinimid**:

$$\begin{matrix} CH_2.COOH \\ | \\ CH_2.COO(NH_4) \end{matrix} = \begin{matrix} CH_2.CO\diagdown \\ | \qquad NH + 2H_2O, \\ CH_2.CO\diagup \end{matrix} \quad \text{or} \quad \begin{matrix} CH_2.COOH \\ | \\ CH_2.CO.NH_2 \end{matrix} = \begin{matrix} CH_2.CO\diagdown \\ | \qquad NH + H_2O. \\ CH_2.CO\diagup \end{matrix}$$

Conversely the imids, when acted upon by alkalies or baryta water, are converted into salts of the amic acids:

$$\begin{matrix} CH_2.CO\diagdown \\ | \qquad NH \\ CH_2.CO\diagup \end{matrix} + KHO = \begin{matrix} CH_2.COOK \\ | \\ CH_2.CO.NH_2. \end{matrix}$$

The **primary monamids** of the fatty acids are solid, crystallizable, neutral in reaction, volatile without decomposition, mostly soluble in alcohol and ether, and mostly capable of uniting with acids to form compounds similar in constitution to the ammoniacal salts. They are capable of uniting with $H_2O$ to form the ammoniacal salts of the corresponding acids, and with the alkaline hydroxids to form the metallic salts of the corresponding acids and ammonia. The **secondary monamids**, containing two radicals of the fatty series, are acid in reaction, and their remaining atom of extra-radical hydrogen may be replaced by an electro-positive atom.

**Formamid**—$CHO.NH_2$—45—is a colorless liquid, soluble in $H_2O$ and in alcohol, boils at 192°–195° (377.6°-385° F.), suffering partial decomposition, obtained by heating ethyl formate with an alcoholic solution of ammonia, or by the dry distillation of ammonium formate. It is decomposed by dehydrating agents, with formation of hydrocyanic acid. **Mercury formamid** is obtained in solution by gently heating freshly-precipitated mercuric oxid with $H_2O$ and formamid.

Under the name **chloralamid** a compound, formed by the union of chloral and formamid, and having the constitution, $CCl_3CH\langle^{OH}_{NHCHO}$, has been used as a hypnotic. It forms colorless, odorless, faintly bitter crystals, fusible at 115° (239° F.), sparingly soluble in water. It is decomposed by alkalies, chloroform and ammonia being among the products of the decomposition. It is not affected by acids.

**Chloralimid**—$CCl_3.C\begin{matrix}\diagup NH \\ \diagdown H\end{matrix}$—**is another related derivative, formed by the action of ammonium acetate upon chloral hydrate, or by the action of heat upon chloral ammonia. It is a crystalline solid, sparingly soluble in water, readily soluble in ether and in alcohol. When heated to 180° (356° F.) it is decomposed into chloroform and formamid.**

**Acetamid**—$CH_3.CO.NH_2$—**is obtained by heating, under pressure, a mixture of ethyl acetate and ammonium hydroxid, and purifying by distillation. It is solid, crystalline, very soluble in $H_2O$, alcohol, and ether; fuses at 82° (179.6° F.); boils at 222° (431.6° F.); has a sweetish, cooling taste, and an odor of mice. Boiling potassium hydroxid solution decomposes it into potassium acetate and ammonia. Phosphoric anhydrid deprives it of $H_2O$, and forms with it acetonitril or methyl cyanid.**

### DIAMIDS.

The diamids correspond to the diamins (p. 330). They are derived from two molecules of ammonia by the substitution of bivalent acid radicals for an equivalent number of hydrogen atoms. Thus, oxamid: $H_2N.(C_2O_2)''.NH_2$; and carbamid, $H_2N.(CO)''.NH_2$.

They are formed: (1) By the action of ammonia upon the neutral esters. Thus ethyl oxalate yields oxamid:

$$\begin{matrix}CO.OC_2H_5 \\ | \\ CO.OC_2H_5\end{matrix} + 2NH_3 = \begin{matrix}CO.NH_2 \\ | \\ CO.NH_2\end{matrix} + 2CH_3.CH_2OH.$$

(2) By heating the neutral ammonium salt of the corresponding acid. Thus ammonium carbonate yields carbamid:

$$OC\begin{matrix}\diagup ONH_4 \\ \diagdown ONH_4\end{matrix} = OC\begin{matrix}\diagup NH_2 \\ \diagdown NH_2\end{matrix} + 2H_2O$$

**Carbamid — Urea** — $H_2N.CO.NH_2$ — **exists in nature in the urine of the mammalia, and, in smaller quantity, in the excrement of birds, fishes and some reptiles; also in the mammalian blood, chyle, lymph, liver, spleen, lungs, brain, vitreous and aqueous humors, saliva, perspiration, bile, milk, amniotic and allantoïc fluids, and in serous fluids.**

Urea is formed by the methods given above; also, (1) as a product of decomposition of uric acid, usually by oxidation. Thus nitric acid oxidizes uric acid to urea and alloxan: $2C_5H_4N_4O_3 + 2H_2O + O_2 = 2CON_2H_4 + 2C_4H_2N_2O_4$. (2) By the hydrolysis of creatin. Thus urea and sarcosin are formed by the action of KHO upon creatin: $C_4H_9N_3O_2 + H_2O = CON_2H_4 + C_3H_7NO_2$. (3) By the action

of carbonyl chlorid upon dry ammonia: $COCl_2+2NH_3=CON_2H_4+2HCl$. (4) By the action of barium hydroxid upon guanidin (p. 335), or upon the hexon bases, lysatin and arginin, products of decomposition of the proteins (p. 499). (5) By atomic transposition of its isomere, ammonium isocyanate, by heat: $O:C:N.NH_4=H_2N.CO.NH_2$.

Urea crystallizes from its aqueous solution in long rhombic prisms or needles. It is colorless and odorless, and has a cooling taste, somewhat resembling that of saltpeter. It is neutral in reaction; soluble in one part of water, in five parts of cold alcohol, and in one part of boiling alcohol, soluble in amylic alcohol, nearly insoluble in ether. It fuses at 132° (269.6° F.).

Heated a few degrees above its fusing point, urea appears to boil, giving off ammonia and ammonium carbonate, and finally leaves a dry, solid residue, consisting of **ammelid**, $C_6H_9N_2O_3$, **cyanuric acid**, $C_3O_3N_3H_3$, and **biuret**, $C_2H_2N_3H_5$. This residue, dissolved in water, gives a fine red-violet color with KHO and $CuSO_4$ (Biuret reaction). When added to a concentrated solution of furfurole and hydrochloric acid, solid urea or urea nitrate, forms a yellow solution, changing in color to green, blue and intense purple-violet. After a time the mixture thickens and blackens (Schiff's reaction).

Dilute aqueous solutions of urea are not decomposed by boiling; but if the solution be concentrated, or the boiling prolonged, or the temperature raised above 100°, the urea is partly decomposed into $CO_2$ and $NH_3$. The same decomposition takes place more rapidly and completely under pressure at 140° (234° F.). It is also caused by bacterial action and by a urinary enzym (see Urine).

Urea is decomposed into carbon dioxid, water and nitrogen by the alkaline hypochlorites and hypobromites, by chlorin and by nitrous acid. Strong acids and alkalies decompose it into carbon dioxid and ammonia.

Urea forms definite compounds, not only with acids, but also with certain salts and oxids. **Urea nitrate**—$H_2N.CO.NH_3.NO_3$—forms, in white crystals, when a concentrated solution of urea is treated with nitric acid in the cold. It is much less soluble than urea, especially in presence of an excess of nitric acid. It is decomposed by evaporation of its solutions. **Urea oxalate**—$CO:(NH_3)_2:O_4C_2$—separates as a fine, crystalline powder, from mixed concentrated aqueous solutions of urea and oxalic acid. Its solution may be evaporated without decomposition.

When solutions containing molecular weights of urea and sodium chlorid are evaporated, prismatic crystals, containing $CON_2H_4$, $NaCl+H_2O$ are obtained. Urea forms several compounds with mercuric oxid. Of these, the compound $(CON_2H_4)_2$, 4HgO, containing 72 parts of HgO for 10 parts of urea, is formed as a white,

amorphous precipitate when a dilute solution of mercuric nitrate is gradually added to a dilute, alkaline solution of urea, and the excess of acid neutralized from time to time.

### THIOUREA AND THIOCARBAMIC ACIDS.

The thio-compounds, corresponding to carbamic acid (p. 346) and to urea, in which oxygen is replaced by sulfur, exist either in their own forms or in their derivatives. Thus:

Thiocarbamic acid. Sulfocarbamic acid. Dithiocarbamic acid. Thiourea.

**Thiocarbamic acid and sulfocarbamic acid are known only in their esters. Dithiocarbamic acid** may be obtained by decomposition of its ammonium salt, which is produced by the action of ammonia in alcoholic solution upon carbon disulfid: $CS_2 + 2NH_3 = S:C\langle^{S(NH_4)}_{NH_2}$. Similarly, the amin salts of the alkyl-dithiocarbamic acids are formed by the action of the primary amins upon carbon disulfid (p. 343).

**Thiourea** may be obtained by the action of heat upon ammonium isothiocyanate: $S:C:N(NH_4) = S:C\langle^{NH_2}_{NH_2}$, as urea is obtained from the isocyanate (p. 349). It is also formed by the action of hydrogen sulfid upon cyanamid (p. 344): $H_2S + CN.NH_2 = S:C\langle^{NH_2}_{NH_2}$. It is decomposed by boiling acids or alkalies into $CO_2$, $NH_3$, and $H_2S$. It forms salts, and alkyl, phenyl and acidyl derivatives similar to those of urea.

### COMPOUND UREAS.

These compounds, which are exceedingly numerous, may be considered as derived from urea by the substitution of one or more alcoholic or acid radicals for hydrogen atoms.

Those containing alcoholic radicals, **alkyl ureas**, such as ethyl urea, $CO\langle^{NH_2}_{NH.C_2H_5}$, are obtained: (1) By the action of primary or secondary amins upon isocyanic esters: $NH_2.C_2H_5 + O:C:N.C_2H_5 = CO:(NH.C_2H_5)_2$. (2) By heating the isocyanic esters with water, the amins and carbonic acid being formed as intermediate products: $OC:N.C_2H_5 + H_2O = NH_2.C_2H_5 + CO_2$, and $OC:N.C_2H_5 + NH_2.C_2H_5 = CO:(NH.C_2H_5)_2$.

Those containing acid radicals have received the distinctive name of **ureïds**. Of these, some are **monureïds**, derived from a single molecule of urea, others **diureïds**, derived from two molecules. Some

of the monureïds are open chain compounds, but the most important of them, and all the diureïds are cyclic compounds. Thus there are two ureïds, corresponding to glycollic acid, $\begin{matrix}CH_2OH\\|\\COOH\end{matrix}$ : one, **hydantoïc acid**, an open chain ureïd: $CO\langle^{NH_2}_{NH.CH_2.COOH}$; the other, **hydantoïn**, a cyclic compound: $CO\langle^{NH.CH_2}_{NH.CO.}$

The **monacidyl monureïds**, containing a single acidyl, are formed by the action of acidyl chlorids or anhydrids upon urea. Thus acetyl-urea is obtained with acetyl chlorid: $CH_3.CO.Cl+NH_2.CO.NH_2 = H_2N.CO.NH(CO.CH_3) + HCl$, or with acetic anhydrid: $(CO.CH_3)_2,O + 2NH_2.CO.NH_2 = 2NH_2.CO.NH(CO.CH_3) + H_2O$. **Mixed ureids**, containing an alkyl and an acidyl, are formed in like manner from alkyl-ureas. Thus methyl-urea and acetyl chlorid form methyl-acetyl-urea: $CH_3.NH.CO.NH_2 + CH_3.CO.Cl = CH_3.NH.CO.NH(CO.CH_3)+HCl$. Such mixed ureïds are also formed by the action of bromin and potassium hydroxid upon the amids, by reactions comparable with those which give rise to the formation of the monamins (p. 327). Thus methyl-acetyl-urea is formed from acetamid: $2CH_3.CO.NH_2+Br_2+2KHO = CH_3.HN.CO.NH(CO.CH_3)+2KBr+2H_2O$.

The **diacidyl-ureïds** are formed by the action of phosgene (carbonyl chlorid) upon the amids. Thus acetamid yields diacetyl-urea: $2CH_3.CO.NH_2 + COCl_2 = (CH_3.CO)HN.CO.NH(CH_3.CO)+2HCl$.

**Allophanic Acid**—$CO\langle^{NH_2}_{NH.COOH}$—the simplest of the open chain monureïds, derived from carbonic acid: $CO:(OH)_2$, is known in its esters only. The corresponding derivative of carbamic acid: $CO\langle^{NH_2}_{OH}$, is **biuret**, $CO\langle^{NH_2}_{NH.CO.NH_2}$, formed by heating the allophanic esters with ammonia, or by heating urea to 150°–160° (p. 349).

**Glycolyl Urea—Hydantoïn**—$CO\langle^{NH.CH_2}_{NH.CO}$, the simplest of the cyclic monureïds, is formed by the action of hydriodic acid upon allantoïn (p. 353), or upon alloxanic acid (p. 353). It is converted into the corresponding open chain compound, **hydantoïc, or glycoluric acid**, $CO\langle^{NH_2}_{NH.CH_2.COOH}$, by heating with barium hydroxid.

Corresponding to hydantoïn are a number of substituted hydantoïns (its superior homologues), constituted by substitution of alkyl groups for the remaining hydrogen. They differ according as the substitution is in the $CH_2$ group ($\alpha$); in the NH group between the $CH_2$ and CO ($\beta$); or in the NH between the two CO groups ($\gamma$). The $\beta$ compounds are formed by heating the monoalkyl amido acids

(p. 363) with urea. Thus urea and sarcosin (p. 364) yield β methyl hydantoïn:

$$CO(NH_2)_2 + \begin{matrix} CH_2(NH.CH_3) \\ | \\ COOH \end{matrix} = CO\begin{matrix} N(CH_3).CH_2 \\ NH.CO \end{matrix} + NH_3 + H_2O.$$

**Oxalyl Urea—Parabanic acid**—$CO\begin{matrix} NH.CO \\ | \\ NH.CO \end{matrix}$—is produced by oxidation of uric acid, or of alloxan by nitric acid; or is formed synthetically by the action of phosphorus oxychlorid upon a mixture of urea and oxalic acid. Its salts are converted into oxalurates by water.

**Oxaluric Acid**—$CO\begin{matrix} NH_2 \\ NH.CO.COOH \end{matrix}$—occurs in its ammonium salt in the urine in small amount. It is formed from oxalyl urea as indicated above, or by the action of bromin, or by heating with calcium carbonate. The free acid is a white, crystalline powder, sparingly soluble in water. It is readily decomposed into urea and oxalic acid by heating with alkalies or even with water.

**Malonyl Urea — Barbituric acid** — $CO\begin{matrix} NH.CO \\ NH.CO \end{matrix}CH_2$— is formed by the action of concentrated sulfuric acid upon alloxantin (p. 354), and is produced synthetically by the action of phosphorus oxychlorid upon a mixture of malonic acid and urea at 100° (212° F.).

**Nitromalonyl Urea** — $CO\begin{matrix} NH.CO \\ NH.CO \end{matrix}CH.NO_2$ — is formed by the action of fuming $HNO_3$ on malonyl urea. It behaves as a tribasic acid.

**Amidomalonyl Urea**—$CO\begin{matrix} NH.CO \\ NH.CO \end{matrix}CH.NH_2$—is formed by reduction of nitromalonyl urea by hydriodic acid. It yields murexid when boiled with ammonia; and is converted into alloxan by nitrous acid. It is the parent of a number of derivatives, called uramils, constituted by substitution of alkyl groups for the remaining hydrogen atoms.

**Pseudouric Acid**—$CO\begin{matrix} NH.CO \\ NH.CO \end{matrix}CH.NH.CO.NH_2$—which differs in composition from uric acid by $+H_2O$, is produced as its ammonium salt, by heating urea and amidomalonyl urea together at 180° (356° F.). By dehydration by heating with oxalic acid to 145° (293° F.) it yields uric acid.

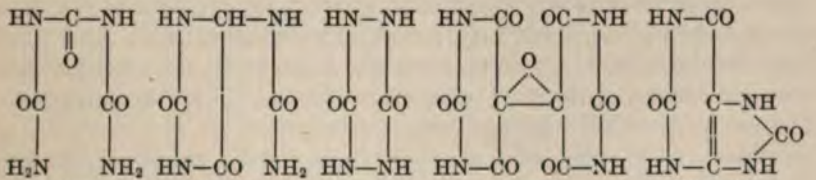
**Tartronyl Urea—Dialuric acid**—$CO\begin{matrix} NH.CO \\ NH.CO \end{matrix}CH.OH$—is produced along with oxaluric acid, by reduction of alloxan. Nitrous acid converts it into allantoïn.

**Mesoxalyl Urea—Alloxan**—$CO\begin{matrix} NH.CO \\ NH.CO \end{matrix}CO$—is a product of the limited oxidation of uric acid or of alloxantin. It has been found in the intestinal mucus in diarrhœa. It forms prismatic crystals, readily soluble in water, which turn red in air, are acid in reaction, and stain

the skin red. Reducing agents convert it into alloxantin, or into tartronyl urea, and by oxidation it yields oxalyl urea. Heated with barium hydroxid it yields **alloxanic acid**: $CO\langle^{NH_2}_{NH.CO.COOH}$.

**Methyl Uracyl**—$CO\langle^{NH.C(CH_3)\diagdown}_{NH.CO.\!-\!-CH}$—is the methyl derivative of the unknown monureïd **uracyl**, produced by the interaction of urea and acetoacetic ester: $CO\langle^{NH_2}_{NH_2} + \begin{matrix}CO.CH_3\\ |\\ CH_2.COO(C_2H_5)\end{matrix} = CO\langle^{NH.C(CH_3)\diagdown}_{NH.CO\!-\!-CH} +$ $CH_3.CH_2OH + H_2O$. It is formed as one of the steps in a synthesis of uric acid.

**Diureïds**—may be considered as formed by the fusion of two monureïd molecules, as alloxantin is produced by the fusion of two alloxan molecules, with elimination of an atom of oxygen. Or they may be regarded as formed by the union of two molecules of urea, with elimination of hydrogen, and the introduction of a group of equivalent valence, except in the case of diurea, in which the union is direct. Considered in this latter light, the diureïds may be classified into three groups: (1) those formed by fusion of two molecules of urea, with elimination of $H_2$, and the introduction of a bivalent group, as **carbonyl diurea**, a crystalline substance, formed by the action of phosgene upon urea: $2H_2N.CO.NH_2 + COCl_2 = (H_2N.CO.NH)_2CO + 2HCl$; (2) those formed by elimination of $H_3$, and introduction of a trivalent group, as in allantoïn, $(HN.CO.NH):CH.CO.(HN.CO.NH_2)$; (3) those whose formation is attended with elimination of $H_4$. This group may be further subdivided into: (*a*) those formed by direct union of the two urea remainders: **diurea**, $CO\langle^{NH.NH\rangle}_{NH.NH/}CO$, a cyclic derivative of hydrazin, $H_2N.NH_2$; (*b*) those in which the two urea remainders are symmetrically attached by introduction of a quadrivalent group, as alloxantin, and (*c*) those in which the attachment is unsymmetrical, as in uric acid. The constitution of these several compounds is illustrated by the following formulæ:




**Allantoïn**—$C_4H_6N_4O_3$—a diureïd derived from glyoxylic acid (p. 297), occurs in the allantoïc fluid of the cow, in the urine of sucking calves, of dogs and cats fed on meat, of children during the first eight days of life, of adults after administration of tannin, and of

pregnant women; also in beet-juice. It is formed by oxidizing uric acid by lead peroxid, or potassium permanganate in alkaline solution. Also by heating together urea and glyoxylic acid at 100° (212° F.), or, similarly from urea and mesoxalic acid (p. 298). It crystallizes in prisms, tasteless, neutral, sparingly soluble in cold water, readily soluble in hot water or in alcohol. Warmed with barium hydroxid, or with lead peroxid, it forms allanturic acid: $CO\begin{matrix}/NH.CH.OH. \\ \\ \backslash NH.CO\end{matrix}$ Heated with alkalies it is decomposed into oxalic acid and ammonia.

**Alloxantin**—$C_8H_4N_4O_7$—is formed by the action of reducing agents upon alloxan, or by the oxidation of uric acid. It forms sparingly soluble prisms, which turn red on exposure to air. It is derived from alloxan as indicated above.

**Murexid**—is the ammonium salt of the unknown **purpuric acid**, $C_8H_5N_5O_6$, derived from alloxantin by substitution of NH for O. It is a purple substance, produced by heating alloxantin in ammonia, or by evaporating nitric acid on uric acid, and adding ammonia to the residue (murexid reaction).

## URIC ACID AND THE XANTHIN BASES.

In this group are included a number of substances of great physiological interest: uric acid, xanthin, hypoxanthin, guanin, and their derivatives, as well as the so-called alkaloids caffein and theobromin.

**Uric Acid** — *Lithic acid* — *Trioxypurin* — $C_5H_4N_4O_3$ — occurs in the urine of man and of the carnivora, in combination, chiefly as its disodic salt; in the urine of the herbivora, in which ordinarily it is replaced by hippuric acid, when, in early life and during starvation, they are, for the time being, practically carnivora; in some urinary calculi, in the so-called "chalky deposits," or "tophi," in the joints of the gouty; very abundantly in the excretions of serpents, tortoises, birds, molluscs, and insects, and in guano; in smaller amount in the blood, spleen, lungs, liver, pancreas, brain and muscular fluid. It is best obtained from guano or from the solid urine of serpents, which consists almost entirely of ammonium urate. It is formed synthetically, as described below.

When pure, uric acid crystallizes in small, colorless, rhombic, rectangular or hexagonal plates, or in rectangular prisms. As crystallized from the urine, it is more or less colored by the urinary pigments, and the angles of the crystals are rounded to produce lozenge shapes, which are arranged in bundles, crosses or daggers. It is almost insoluble in water, requiring for its solution 1,900 parts of boiling water and 15,000 parts of cold water, soluble in 1,900 parts

of a 2 per cent. solution of urea, insoluble in alcohol and in ether. Cold HCl dissolves it more readily than $H_2O$, and on evaporation deposits it in colorless, rectangular plates. Its aqueous solution is acid to test-paper, but tasteless and odorless. It also dissolves unchanged in concentrated $H_2SO_4$, and is deposited from the solution on dilution with water.

Uric acid is decomposed by heat into ammonia, carbon dioxid, urea and cyanuric acid. Heated with Cl it yields cyanuric acid and HCl. With Cl, Br or I, at the ordinary temperature, it forms oxalic acid, alloxan, parabanic acid and ammonium cyanate. It dissolves in cold $HNO_3$, with effervescence and formation of alloxan, alloxantin and urea; with hot $HNO_3$, parabanic acid is produced. A yellow or red residue remains when $HNO_3$ is evaporated on uric acid; this assumes a fine red-violet or purple color when moistened, in the cold, with $NH_4HO$, NaHO or KHO (murexid reaction). Uric acid is decomposed by sodium hypobromite, giving off 47 per cent. of its N in the cold, or the whole when heated. It reduces the salts of copper on prolonged boiling in alkaline solution. Nascent hydrogen reduces it to xanthin (Constitution, see p. 358).

Uric acid is a weak dibasic acid. The monometallic salts are formed by dissolving the acid in solutions of the metallic carbonates, or by treating solutions of the dimetallic salts with carbon dioxid. The dimetallic salts are formed by dissolving the acid in solutions of the metallic hydroxids, free from carbonate. **Mono-ammonium urate,** $C_5H_3N_4O_3(NH_4)$, exists in the solid urines of the lower animals, and in urinary sediments and calculi. It is very sparingly soluble in water. **Dipotassic urate** is alkaline in taste, absorbs $CO_2$ from the air, and is soluble in 44 parts of cold $H_2O$. **Disodic urate** forms nodular masses, soluble in 77 parts of cold water, and absorbs $CO_2$ from the air. It is probably in this form of combination that uric acid exists normally in the urine. **Monsodic urate** is much less soluble, requiring 1,200 parts of water for its solution. It exists, generally amorphous, in urinary sediments (amorphous urates) and calculi, and in the arthritic deposits of the gouty, sometimes beautifully crystalline. **Monocalcic urate,** soluble in 603 parts of cold water, also occurs occasionally in urinary sediments and calculi, and in "chalk stones." **Monolithic urate,** $C_5H_3N_4O_3Li$, crystallizes in needles, soluble in 60 parts of water at 50° (122° F.), or in 368 parts at 19° (68.2° F.). It is chiefly with a view to the formation of this, the most soluble of the monometallic urates, that the salts of lithium are given to patients suffering from the uric acid diathesis. Two salts of uric acid with organic bases are still more soluble. **Piperazin urate** (p. 462) dissolves in 50 parts of water at 17° (62.6° F.) and **lysidin urate** (p. 333) in 6 parts of water.

**The Xanthin Bases, also called Alloxuric, Purin, or Nuclein Bases, form a series of which uric acid is the most highly oxidized member:**

| | | | |
|---|---|---|---|
| Uric acid, | $C_5H_4N_4O_3$ | Heteroxanthin, | $C_5H_3(CH_3)N_4O_2$ |
| Xanthin, | $C_5H_4N_4O_2$ | Paraxanthin, | $C_5H_2(CH_3)_2N_4O_2$ |
| Hypoxanthin, | $C_5H_4N_4O$ | Theobromin, | $C_5H_2(CH_3)_2N_4O_2$ |
| Guanin, | $C_5H_5N_5O$ | Theophyllin, | $C_5H_2(CH_3)_2N_4O_2$ |
| | | Caffein, | $C_5H(CH_3)_3N_4O_2$ |
| Adenin, | $C_5H_5N_5$ | Epiguanin, | $C_5H_4(CH_3)N_5O$ |
| Carnin, | $C_7H_8N_4O_3$ | Episarkin, | $C_4H_6N_3O$(?) |

The compounds named in the second column are methyl derivatives of those in the first column. The xanthin bases, adenin, guanin, hypoxanthin and xanthin, are products of decomposition of the nucleins, which are themselves produced by decomposition of the nucleoproteids, important constituents of nucleated cells. They may, therefore, be considered as intermediate products of oxidation in the formation of uric acid, and, to some extent at least, of urea in the animal body.

**Xanthin** —*Xanthic acid* —*Urous acid*—2-6-*Dioxypurin*—$C_5H_4N_4O_2$ —occurs in a rare form of vesical calculus; in the pancreas, spleen, liver, thymus, kidneys and brain, and in the melt of fishes. It is a constant constituent of the urine in small amount. It is formed by the action of nitrous acid upon guanin, and by the action of nascent hydrogen upon uric acid.

It is usually amorphous, but may form rhombic plates. It is very sparingly soluble in water, insoluble in alcohol or ether, readily soluble in alkalies. Its ammoniacal solution gives a gelatinous precipitate with silver nitrate. If dissolved in nitric acid and the solution evaporated, xanthin leaves a yellow residue, which, when moistened with KHO solution, turns reddish-yellow, and violet-red when heated. Heated to 100° (212° F.) with methyl iodid, it is converted into theobromin. When chlorin water and a trace of $HNO_3$ are evaporated with xanthin, and the residue is exposed to ammonia, it assumes a red or purple color (Weidel's reaction).

**Hypoxanthin** — *Sarkin* — 6-*Oxypurin* — $C_5H_4N_4O$ — occurs in the same situations as xanthin; also in notable quantity in the blood and urine in leukæmia, and in the melt of the salmon and carp. It also occurs in numerous seeds and pollen of plants, and is produced during putrefaction of proteins. It is a product of the action of the gastric and pancreatic juices, and of dilute acids upon fibrin. It is produced by the action of nitrous acid upon adenin, by the action of sodium amalgam upon uric acid or xanthin, and by the decomposition of some nucleins by acids.

It crystallizes in small, colorless needles, soluble in 300 parts of cold water, or in 75 parts of boiling water; soluble in acids and in

alkalies. Its ammoniacal solution forms a precipitate with silver nitrate. Nitrous acid oxidizes it to xanthin. It does not give Weidel's reaction. When acted on by zinc and HCl, and then treated with excess of alkali, it forms a ruby-red solution, which turns brown-red (Kossel's reaction).

**Guanin** — 2-*Imido*-6-*oxypurin* — $C_5H_5N_5O$ — occurs abundantly in guano, and as the principal constituent of the excrement of spiders; in less amount in the spleen, liver, pancreas and testicles; in the melt of the salmon; in the scales and swimming bladders of certain fish; in normal urine in traces; in the blood in leukæmia; and in the young leaves and pollen of certain plants.

It is a white or yellowish, amorphous, tasteless and odorless powder; almost insoluble in water, alcohol and ether; readily soluble in acids and in alkalies. It forms crystalline precipitates with silver nitrate and with picric acid. It gives the xanthin reaction with $HNO_3$ and KHO. Nitrous acid oxidizes it to xanthin. Hydrochloric acid and potassium chlorate oxidize it to guanidin (p. 335), oxalylurea (p. 352) and $CO_2$. It does not respond to Weidel's reaction.

**Adenin** — 6-*Amido-purin* — $C_5H_5N_5$ — exists widely disseminated in all nucleated cells, most abundantly in carp-melt and in the thymus gland. It occurs in the blood and urine in leukæmia, and also exists in yeast and abundantly in tea leaves.

It crystallizes in nacreous plates, or in long needles, containing 3 Aq., which they lose only at 110° (230° F.), although they suddenly become opaque at 53° (127.4° F.), a property characteristic of adenin. Very soluble in hot water, it requires 1,086 parts of cold water for its solution. It is insoluble in cold alcohol, ether and chloroform; readily soluble in acids and alkalies, with which it forms compounds. Its solubility in ammonia is less than that of hypoxanthin, but greater than that of guanin. It forms crystalline, difficultly soluble compounds with silver nitrate and with picric acid. It is not reddened by warming with $HNO_3$ and moistening the residue with alkali; does not respond to Weidel's reaction, and behaves like hypoxanthin towards Kossel's reaction. Nitrous acid oxidizes it to hypoxanthin. Heated to 200° (392° F.) with HCl, it forms glycocoll, ammonia, formic acid and carbon dioxid. Fused with KHO it produces potassium cyanid.

**Carnin** — $C_7H_8N_4O_3$ — is obtained from Liebig's meat extract, and has also been found in the muscular tissue of fish and of frogs, and in the urine. It is isomeric with the dimethyl-uric acids. It forms chalky, microscopic crystals, readily soluble in hot water, sparingly soluble in cold water, insoluble in alcohol and ether. It forms compounds with acids and with alkalies, similar to those of hypoxanthin. Chlorin, bromin and nitrous acid convert it into hypo-

xanthin by elimination of the elements of acetic acid. It does not respond to the Weidel reaction.

**Heteroxanthin** — *7-Methyl-xanthin* — $C_6H_8N_4O_2$ — occurs in small quantity in the urine, accompanied by 1-methyl-xanthin, paraxanthin, or 1-7-dimethyl-xanthin, epiguanin, or 7-methyl-guanin, and episarkin, a xanthin base of undetermined constitution. With the Weidel reaction, heteroxanthin, 1-methyl-xanthin and paraxanthin respond; episarkin and epiguanin do not. With the xanthin reaction ($HNO_3$ and NaHO) 1-methyl-xanthin gives an orange color, and epiguanin a red color. The others are negative.

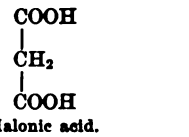
**Theobromin** — 3-7-*dimethyl-xanthin* — $C_7H_8N_4O_2$ — occurs in the seed of *Theobroma cacao* in the proportion of about 2 per cent. It is a crystalline powder, bitter in taste; difficultly soluble in water, alcohol, ether, and chloroform; soluble in acids, with which it forms salts; soluble in $NH_4HO$. By partial demethylation it yields heteroxanthin. With silver nitrate it forms a crystalline precipitate, which, heated with methyl iodid, yields caffein. When treated with chlorin water and gradually evaporated, it leaves a red-brown residue, which turns purple with $NH_4HO$.

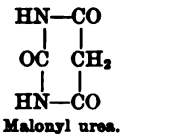
**Theophyllin** — 1-3-*dimethyl-xanthin* — $C_7H_8N_4O_2$ — occurs in tea extract, and is formed from 1-3-dimethyl-uric acid.

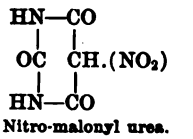
**Caffein**—*Thein*—*Guaranin*—1-3-7-*trimethyl-xanthin*— $C_8H_{10}N_4O_2$ —exists in coffee, tea, Paraguay tea, guarana, and other plants, and may be produced from 1-3-7-trimethyl-uric acid. It crystallizes in long, silky needles; faintly bitter; soluble in 75 parts $H_2O$ at 15° (59° F.); less soluble in alcohol and ether. It gives the same reaction with chlorin water and $NH_4HO$ as theobromin. With $HNO_3$, evaporation and addition of $NH_4HO$, it gives a purple color.

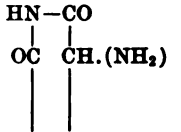
**Methyl-uric Acids.**—The four hydrogen atoms of uric acid are replaceable by methyl groups, forming three mono-, four di-, two tri-, and one tetra-methyl uric acids. These compounds, in which the methyls are attached to the nitrogen atoms, are produced by the action of methyl iodid upon urates or upon methyl-pseudouric acids.

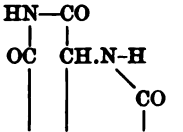
**Synthesis and Constitution of Uric Acid and the Xanthin Bases.**—The synthesis of uric acid has been accomplished by several methods, starting from acetic acid and urea, through monochloracetic acid or aceto-acetic acid (p. 298). Two of the simplest are the following: (1) Amido-acetic acid (p. 363), when heated with urea, forms uric acid (disregarding intermediate products) according to the equation: $CH_2(NH_2).COOH+3NH_2.CO.NH_2=C_5H_4N_4O_3+2H_2O+3NH_3$; (2) Malonic acid is produced from mono-chloracetic acid (p. 288). From this malonyl urea, nitro-malonyl urea, amido-malonyl urea, pseudo-uric acid and uric acid are successively obtained by the methods given on p. 352:

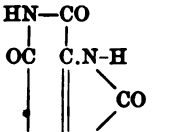

Malonic acid.


Malonyl urea.

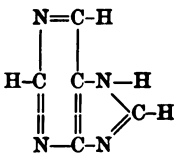

Nitro-malonyl urea.

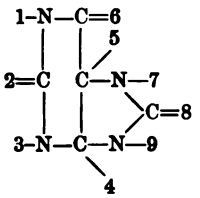

Amido-malonyl urea.

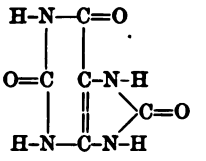

Pseudouric acid.

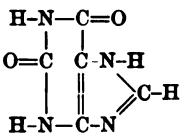

Uric acid.

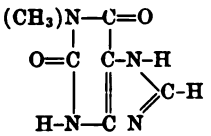
Uric acid and the xanthin bases are considered as derivatives of a hypothetical compound, called **purin**, and having the composition $C_5N_4H_4$ (see formula below). If all the double linkages in this formula be converted into single ones there remain three bivalent positions, 2, 6, and 8, in the second formula below, and six univalent positions: 1, 3, 4, 5, 7, and 9. Or if the double linkage between 4 and 5 be retained, as it is in all the known compounds of this group, there are four univalent positions, which in uric acid are filled by hydrogen atoms, while the bivalent positions are occupied by oxygen atoms. The structural formulæ of the members of the xanthin group, considered as derivatives of purin, are as follows:

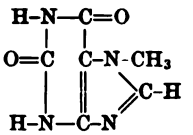

"Purin."

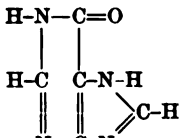


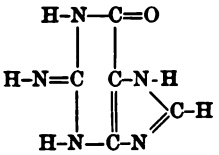

Uric acid (Trioxypurin).

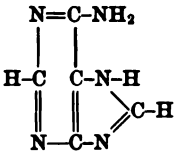

Xanthin
(2-6-Dioxypurin).


1-Methyl xanthin.


Heteroxanthin
(7-Methyl xanthin).


Hypoxanthin
(6-Oxypurin).


Guanin
(2-Imido-6-oxypurin).


Adenin
(6-Amidopurin).

## NITROGEN DERIVATIVES OF ALCOHOLS, ALDEHYDES, AND KETONES.

**Nitro derivatives** of the alcohols, aldehydes, and ketones in which the $NO_2$ is substituted for OH or for O, such as $CH_3.CH_2(NO_2)$, $CH_3.CH(NO_2)_2$ and $CH_3.C(NO_2)_2.CH_3$ are mono- or dinitro-paraffins (p. 325). Besides these, **nitro alcohols** are also known, in which the $NO_2$ is substituted in a hydrocarbon group, e. g., **nitro ethyl alcohol** $CH_2(NO_2).CH_2OH$.

**Amido alcohols**, such as **amido ethyl alcohol**, or **oxethylamin**, $CH_2OH.CH_2(NH_2)$, may also be considered as derived from the glycols by substitution of $NH_2$ for OH. These are the **oxyalkyl bases, oxyamins, or hydramins**, among which are cholin and neurin (p. 329).

**Aldehyde-ammonia**—$CH_3.CH\langle^{OH}_{NH_2}$—is produced by the action of dry $NH_3$ upon an ethereal solution of aldehyde. It is a crystalline solid, soluble in water, fusible at 80° (176° F.). The corresponding compound derivable from formic aldehyde: $H.CH\langle^{OH}_{NH_2}$, is not known; but when formaldehyde and ammonia react, **hexamethylenetetramin** $(CH_2)_6N_4$, is produced: $6CH_2O+4NH_3=(CH_2)_6N_4+6H_2O$.. This is a crystalline solid, very soluble in water, which decomposes when heated, and behaves as a monacid base. It is used as a diuretic and solvent of uric acid, under the name "*formin*."

**Amido aldehydes**, such as **amido acetaldehyde**, $CH_2(NH_2).CHO$, are also known.

The **aldoxims** are derived from the aldehydes by substitution of the **oxim** group $(N.OH)''$ (p. 335) for the oxygen of the aldehyde. Thus **acetoxim**, $CH_3.CH:N.OH$, corresponds to acetic aldehyde, $CH_3.CHO$. They are formed as colorless liquids, miscible with water, by the action of hydroxylamin upon the aldehyde: $H_2N.OH+CH_3.CHO=CH_3.CH.N.OH+H_2O$. The aldoxims are hydrolized into aldehyde and hydroxylamin by boiling with acids: $CH_3.CH:N.OH+H_2O=HO.NH_2+CH_3.CHO$. They form nitrils by the action of acidyl chlorids or anhydrids. Thus acetoxim yields acetonitril and acetic acid: $CH_3.CH:NOH+CH_3.COCl=CH_3.CN+CH_3.COOH+HCl$, or $CH_3.CH:NOH+(CH_3.CO)_2O=CH_3.CN+2CH_3.COOH$.

**Aldehyde hydrazones**—are formed by the action of hydrazins upon aldehydes. Thus **acetaldehyde hydrazone** is formed from acetic aldehyde and phenylhydrazin: $CH_3.CHO+H_2N.NH.C_6H_5=CH_3.CH:N.NH.C_6H_5+H_2O$. (See also p. 429).

**Acetonamins.**—The action of ammonia upon acetone causes a condensation of two or three molecules of acetone, with formation of **diacetonamin**: $^{CH_3.CO.CH}_{(CH_3)_2}\!\!\diagup\!\!\diagdown C.NH_2$, a colorless liquid; and **triaceto-**

**namin**: $OC\langle^{CH_2.C(CH_3)_2}_{CH_2.C(CH_3)_2}\rangle NH$, a crystalline solid, fusible at 40° (104° F.). **Amido-acetones, or amido-ketones,** such as $CH_3.CO.CH_2.NH_2$, **amidoacetone,** are also known.

**Ketoxims, or acetoxims,** are compounds corresponding to the aldoxims, formed by the substitution of the oxim group, N.OH for the oxygen of the acetone. They are formed by the action of hydroxylamin upon an alkaline solution of the acetone. Thus acetone yields acetoxim: $CH_3.CO.CH_3+HO.N:H_2=CH_3.C(NOH).CH_3+H_2O$, a crystalline solid, fusible at 60° (140° F.), which, by the action of nascent hydrogen, is converted into isopropylamin: $CH_3.C(NOH).CH_3+2H_2=(CH_3)_2.CH.NH_2+H_2O$. This constitutes a general method for the formation of the primary amins. With acidyl chlorids they do not form nitrils as do the aldoxims, but the acid radical replaces the hydroxyl hydrogen: $(CH_3)_2C:N.OH+CH_3.COCl=(CH_3)_2C:NO(CO.CH_3)+HCl$.

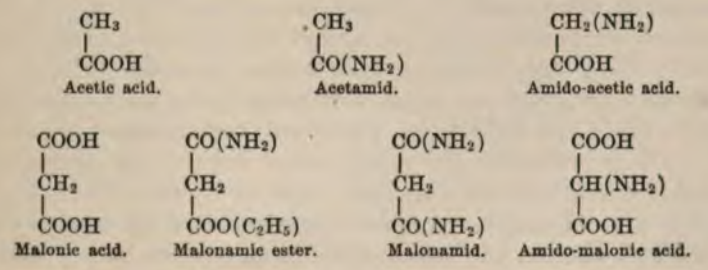
## NITROGEN DERIVATIVES OF ACIDS—NITRO-ACIDS—AMIDO ACIDS—LACTAMS.

The **nitro-acids,** such as **nitro-acetic acid,** $CH_2(NO_2).COOH$, are unstable compounds, usually existing only in their esters.

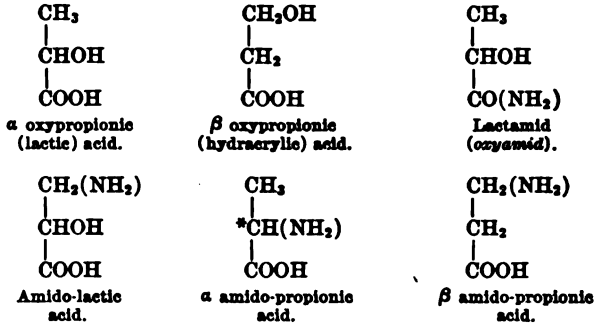
The **amido-acids** are much more stable, and include a number of substances of considerable physiological interest.

The amido-acids are derived by substitution of the amido group, $NH_2$, for hydrogen in a hydrocarbon group of the acid. In this position the attachment of the amido group is much firmer than in the primary amids (p. 345), in which it replaces the hydroxyl. The amids are easily hydrolized by boiling water, with formation of ammonium salts, while the amido-acids suffer no decomposition under like treatment.

From the pure carboxylic acids (p. 277), amic acids (p. 346), amids (p. 345) or amido-acids are derivable by substitution of $NH_2$ for OH or for H:



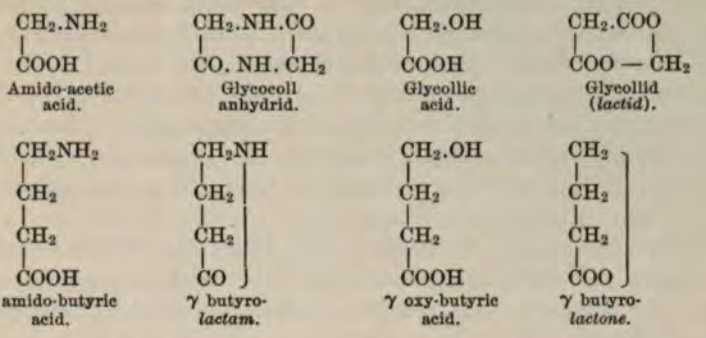
From the monocarboxylic oxyacids (p. 290), **oxyamids** are derived by substitution of $NH_2$ for OH in COOH; amido-acids of the same series by its substitution for H in a hydrocarbon group; and amido-acids of the acetic series by its substitution for OH in a CHOH or a $CH_2OH$ group:



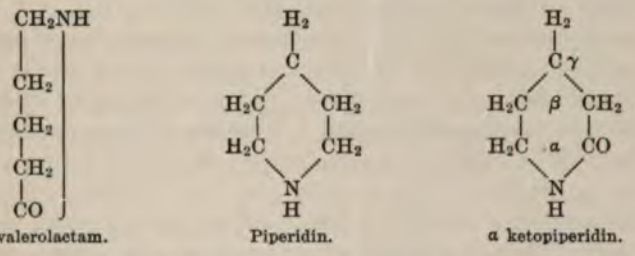

The first amido-acid of the fatty series, **amido-formic acid**, $NH_2.CO.OH$, is carbamic acid (p. 346). The third and superior terms of the series form place isomeres, according to the position of the $NH_2$ group, corresponding to the oxyacids and similarly designated (p. 290) as $\alpha$, $\beta$, $\gamma$, etc., or 1-, 2-, 3-, etc. The fatty amido-acids are also known as **glycocolls** or **alanins**. They are obtained: (1) By the action of ammonia upon the monochloro acids. Thus amido-acetic acid is obtained from monochloracetic acid: $CH_2Cl.COOH+NH_3=CH_2(NH_2).COOH+HCl$. (2) By reduction of the nitro-acids. Thus nitroacetic ester, $CH_2(NO_2).COO.C_2H_5$, yields amido-acetic acid. (3) By the action of nascent hydrogen upon the cyan-fatty acids: $CN.COOH+2H_2=CH_2(NH_2).COOH$.

The amido-acids are crystalline solids, most of which are sweet in taste, soluble in water, insoluble in alcohol or in ether, neutral in reaction. As they contain both amido and carboxyl groups, they have both basic and acid functions. With acids they form ammonium salts. They form stable metallic salts with bases, but their esters are unstable. Stable compounds are, however, produced by the replacement of their amido hydrogen, either by acidyls or by alkyls. The acidyl compounds, such as **acetyl amido-acetic acid**, $CH_2.NH(C_2H_3O).COOH$, are formed by the action of acidyl chlorids upon the amido-acids; and the alkyl derivatives, such as **methyl glycocoll**, $CH_2.NH(CH_3).COOH$, by the action of amins upon haloid fatty acids. On dehydration the amido-acids behave like the oxyacids (pp. 291, 320), which are also both basic and acid. The $\alpha$ acids on dehydration yield cyclic anhydrids, corresponding in constitution to the lactids. The $\gamma$ and $\delta$ acids yield cyclic esters, called **lactams**,

corresponding to the lactones. The resemblance of these compounds is shown by the following formulæ:




The formation of the lactams is another instance of the production of closed chain from open chain compounds (pp. 320, 334). **Delta valerolactam** is α keto-piperidin, or α oxypiperidin (p. 461):




**Amido-acetic Acid**—*Glycocoll—Glycin—Glycolamic acid—Gelatin sugar*—$CH_2.NH_2.COOH$—was first obtained by the action of $H_2SO_4$ upon gelatin. It is also formed by the action of KHO upon glue; and, synthetically, by the methods given above and by the union of formic aldehyde, hydrocyanic acid and water: $H.CHO+HCN+H_2O=CH_2(NH_2).COOH$. It is produced, along with benzoic acid, in the decomposition of hippuric acid (p. 425); as a product of decomposition of glycocholic acid; and by the action of hydriodic acid upon uric acid (p. 358). It has been found uncombined only in the muscle of the scallop.

It appears as large, colorless, transparent crystals; has a sweet taste; fuses at 170° (338° F.); sparingly soluble in cold water; much more soluble in warm water; insoluble in absolute alcohol and in ether.

It forms crystalline salts with acids, which are decomposed at a boiling temperature. Nitric acid oxidizes it to glycollic acid. Its acid function is more marked; it expels carbonic and acetic acids from

calcium carbonate and lead acetate. It dissolves cupric hydroxid in alkaline solution, and there is no reduction on boiling the solution; but on addition of alcohol to the cold solution, blue crystalline needles of copper glycolamate separate. With ferric chlorid it gives an intense red color, which is discharged by acids, and restored by ammonia. With phenol and sodium hypochlorite it gives a blue color, as does ammonia. It forms esters and amids. Its methylic ester is isomeric with sarcosin. Heated under pressure with benzoic acid it forms hippuric acid. Fused with urea it forms glycolylurea (p. 351) and, ultimately, uric acid.

**Methyl-glycocoll — Sarcosin** — $CH_2.NH(CH_3).COOH$ — isomeric with alanin and lactamid, is not known to exist as such in animal nature, but it may be obtained from creatin (p. 336) by the action of barium hydroxid:

$$HN{:}C\begin{matrix}\diagup NH_2\\ \diagdown N(CH_3)\end{matrix}.CH_2.COOH + H_2O = CH_2.NH(CH_3).COOH + H_2N.CO.NH_2.$$

It is formed by the action of methylamin upon monochloracetic acid: $CH_2Cl.COOH+CH_3.H_2N=CH_2.NH(CH_3).COOH+HCl$.

It crystallizes in colorless, transparent prisms; very soluble in water; sparingly soluble in alcohol and ether. Its aqueous solution is not acid, and has a sweetish taste. It forms salts with acids, but it is not known to form metallic salts. It unites with cyanamid to form creatin (p. 336); and with cyanogen chlorid to form methyl-hydantoïn (p. 352).

**Amido-propionic Acids—Alanins**—Two are known: $\alpha$ **alanin**, $CH_3.CH(NH_2).COOH$, formed by the reduction of $\alpha$ nitroso-propionic acid; and $\beta$ **alanin**, $CH_2(NH_2).CH_2.COOH$, formed either by the reduction of $\beta$ nitroso-propionic acid, or by the action of ammonia upon $\beta$ iodo-propionic acid. Neither is known to exist in nature.

**Amido-butyric Acids**—$C_4H_9NO_2$—and **Amido-valerianic acids**—$C_5H_{11}NO_2$—are mainly of theoretic interest. **Alpha amido-n-valerianic acid**, $CH_3.CH_2.CH_2.CH(NH_2).COOH$, is a product of oxidation of coniïn. **Delta amido-n-valerianic acid—Butalanin**, $CH_2(NH_2).(CH_2)_3.COOH$, occurs in the pancreas, and is formed as a product of decomposition of fibrin and of certain proteids.

**Amido-caproic Acids—Leucins.**—Twenty-nine isomeric amido acids are derivable from the seven caproic acids; and this number is still further increased by the fact that in many of these the introduction of the amido group renders a carbon atom asymmetric (see formula of $\alpha$ amido-propionic acid, p. 362). The leucin, which is of physiological interest as a product of decomposition of the proteins, is the inactive $\alpha$ **amido-isobutyl-acetic acid**, $(CH_3)_2{:}CH.CH_2.{*}CH(NH_2).COOH$, as is demonstrated by its synthetic formation from

isovaleric aldehyde, $(CH_3)_2$:CH.$CH_2$.CHO. The corresponding dextro-acid has been obtained by the action of *Penicillium glaucum* upon the inactive acid; and the lævo- acid, known as "vegetable leucin" from the vegetable globulin, conglutin.

"Animal leucin" is produced, accompanied by tyrosin (p. 424), in the decomposition of proteins by boiling with dilute acids or alkalies, by fusion with caustic alkalies, by putrefaction, and by trypsin digestion. It appears to exist also as a normal constituent of the pancreas, spleen, thymus, lymphatic and salivary glands, liver and kidneys. Pathologically the quantity of leucin is much increased in the liver in diseases of that organ, in typhus and in variola; in the bile in typhus; in the blood in leukæmia, and in yellow atrophy of the liver; in the urine in yellow atrophy of the liver, in typhus, in variola, and in phosphorus poisoning; in choleraic discharges from the intestine; in pus; in the fluids of dropsy and of atheromatous cysts.

Leucin crystallizes from alcohol in soft, pearly plates, lighter than water, and somewhat resembling cholesterol; sometimes in rounded masses of closely grouped, radiating needles. Pure leucin is sparingly soluble in water, almost insoluble in alcohol and ether, but readily soluble in hot water or alcohol. When impure it is more soluble. It is odorless and tasteless, and its solutions are neutral. It dissolves readily in acids and alkalies, forming crystalline compounds with the former. It fuses and sublimes at 170° (338° F.) without decomposition, but at a slightly higher temperature is decomposed into amylamin and carbon dioxid.

When heated with hydriodic acid under pressure the leucins are decomposed into ammonia and the corresponding caproic acids. By nitrous acid they are oxidized to the corresponding **oxycaproic, or leucic acids,** $C_6H_{12}O_3$ (p. 293), with elimination of water and of nitrogen. Hot solutions of leucin form precipitates with hot solutions of cupric acetate. They dissolve cupric hydroxid, but do not reduce it on boiling. When boiled with solution of neutral lead acetate and carefully neutralized with ammonia, they deposit brilliant crystals of a compound of leucin and lead oxid. When $HNO_3$ is slowly evaporated in contact with leucin on platinum foil a colorless residue remains, which, when warmed with NaHO solution, turns yellow or brown, and on further concentration, forms oily drops, which do not adhere to the platinum (Scherer's reaction). Solution of leucin, when heated with solution of mercurous nitrate, liberates metallic mercury (Hofmeister's reaction).

**Diamido-fatty acids** have been obtained as products of decomposition of proteins. **Diamido-acetic acid,** $CH(NH_2)_2$.COOH, is produced by boiling proteins with tin and HCl. **Diamido-propionic**

acid, $CH_2(NH_2).CH(NH_2).COOH$, has been obtained synthetically from $\alpha\beta$ dibromo-propionic acid. **Ornithin**, a product of decomposition of ornithuric acid, a substance eliminated by birds after administration of benzoic acid, is probably a **diamido-valerianic acid**, $C_4H_7(NH_2)_2.COOH$. **Lysin**, one of the **hexon bases**, produced in tryptic digestion, and by decomposition of proteins and of protamins, is a **diamido-caproic acid**, $C_5H_9(NH_2)_2.COOH$. (See Proteins.)

**Amido-dicarboxylic Acids** — **Amido-malonic acid**, $COOH.CH(NH_2).COOH$, is a synthetic product which decomposes readily into amido-acetic acid and $CO_2$.

**Amido-succinic Acid—Aspartic acid**—$COOH.CH^*(NH_2).CH_2.COOH$—exists in three optical modifications, of which the lævo-acid is the most important. It is produced during tryptic digestion of proteins, and is a product of their decomposition by dilute acids. It is present in beet-juice vianesse, and is obtained from many vegetable substances as a product of decomposition of its amid, **asparagin**, $CO(NH_2).CH(NH_2).CH_2.COOH$. It crystallizes in rhombic prisms, difficultly soluble in cold water, readily soluble in hot water. Nitrous acid converts it into l-malic acid. It forms a crystalline compound with cupric oxid, which is soluble in hot water, but almost insoluble in cold water.

**Asparagins—Amido-succinic Amids**—The dextro- and lævo-modifications occur together in many plants, in asparagus, and in the sprouts of peas, bean and vetches. Lævo-asparagin, which predominates in nature, crystallizes in rhombic prisms, sparingly soluble in water, odorless, faintly nauseous in taste, faintly acid in reaction. It enters into unstable combination with both acids and bases. Heated with acids or alkalies, it yields aspartic acid and ammonia. Nitrous acid oxidizes it to malic acid, with elimination of N and $H_2O$.

**Amido-glutaric Acid—Glutaminic acid**—$COOH.CH^*(NH_2).CH_2.CH_2,COOH$.—The dextro-acid accompanies aspartic acid as a product of decomposition of proteins and in the vegetables mentioned. It crystallizes in rhombic octahedra, soluble in hot water, insoluble in alcohol and in ether. While the dextro-acid is produced by decomposing proteins by acids, the inactive acid is formed when barium hydroxid is the decomposing agent. It forms a crystalline compound with HCl, which is almost insoluble in the concentrated acid. It forms a crystalline copper salt.

**Amido-thioacids.**—Two amido derivatives of thioacids are of physiological interest:

**Amido-isethionic Acid**—*Amido ethyl-sulfonic acid*—**Taurin**—$\begin{matrix}CH_2.NH_2\\|\\CH_2.SO_3H\end{matrix}$—the amido derivative of isethionic, or oxyethyl sulfonic

acid (p. 322), $\begin{matrix}CH_2.OH\\|\\CH_2.SO_3H\end{matrix}$, occurs in combination with cholic acid as **taurocholic acid** in the bile (p. 527), from which it may be obtained by decomposition by HCl. It also exists in the intestine, fæces, muscle, blood, liver, kidneys, and lungs. Taurin appears in the urine partly in its own form, and partly combined with carbamic acid as **tauro-carbamic acid**: $NH_2.CO.NH.CH_2.CH_2.SO_3H$. It is formed synthetically by heating together chlorethyl sulfonic acid and ammonia:

$$\begin{matrix}CH_2.Cl\\|\\CH_2.SO_3H\end{matrix} + NH_3 = \begin{matrix}CH_2.NH_2\\|\\CH_2.SO_3H\end{matrix} + HCl.$$

Taurin crystallizes in large, oblique rhombic prisms, soluble in water, insoluble in alcohol and in ether. Boiled with strong alkalies, it yields acetic acid and sulfur dioxid. It forms compounds with metallic oxids. That of mercury is formed by boiling taurin solution with freshly precipitated mercuric oxid, and is white and insoluble. Nitrous acid oxidizes it to isethionic acid, with elimination of N and $H_2O$. It behaves both as a base and as an acid.

**Amido-thiolactic Acid**—$CH_3.C(SH)(NH_2).COOH$—is the probable constitution of **cystein**, a product of decomposition of **cystin**, which is probably **dithio-diamido-dilactic acid.**

$$\begin{matrix}COOH\\CH_3\end{matrix}\!\!\rangle C^*(NH_2).S.S.(NH_2).C^*\!\!\langle\begin{matrix}COOH\\CH_3.\end{matrix}$$

Cystin occurs in the urine and in urinary sediments and calculi. It crystallizes in thin, colorless, six-sided plates, insoluble in water, alcohol, ether, or acetic acid, soluble in mineral acids and in alkalies. It is strongly lævogyrous. Nascent hydrogen converts it into cystein. Its solution in NaHO forms a precipitate with benzoyl chlorid. Heated with $HNO_3$ and evaporated, it leaves a red-brown residue which does not give the murexid reaction. Its HCl solution forms an insoluble precipitate with $HgCl_2$.

## PHOSPHORUS, ANTIMONY, AND ARSENIC DERIVATIVES.

Many organic compounds, similar to those containing nitrogen, in which that element is replaced by phosphorus, antimony, or arsenic, are known. Of these only a few arsenic derivatives require mention.

**Dimethyl Arsin**—$(CH_3)_2HAs$—corresponding to dimethyl amin, $(CH_3)_2HN$, is a colorless liquid, having an intensely disagreeable odor, which ignites spontaneously in air. It may be considered as the hydrid of a radical, $(CH_3)_2As$, which, from the disagreeable odor

and intensely poisonous action of all of its compounds, has received the name **cacodyl** (κακός=evil). As the amins are considered as derived from ammonia by substitution of alkyl groups for the hydrogen, so the compounds of which this is a type are derived from the corresponding hydrogen compounds of phosphorus, antimony, and arsenic, and are called **phosphins, stibins,** and **arsins.**

The parent substance of the arseno-organic compounds is a fuming, foul-smelling liquid, obtained by distilling a mixture of arsenic trioxid and potassium acetate, and called **fuming liquid of Cadet.** The principal constituent of this is **cacodyl oxid, or alkarsin,** $\begin{matrix}(CH_3)_2As\\(CH_3)_2As\end{matrix}\!\!>\!O$, a liquid which boils at 120° (248° F.), insoluble in water, soluble in alcohol and in ether. **Cacodyl, or dicacodyl,** $(CH_3)_2As.As(CH_3)_2$ is a colorless, insoluble liquid, which boils at 170° (338° F.), and ignites spontaneously in air. Cacodyl and all of its compounds are exceedingly poisonous, especially the **cyanid,** an ethereal, volatile liquid the presence of whose vapor in air, even in minute traces, produces symptoms referable both to arsenic and to cyanogen. Probably minute quantities of arsins are formed during the putrefaction of cadavers embalmed with arsenical liquids.

## UNSATURATED ALIPHATIC COMPOUNDS.

In this class are included all open chain carbon compounds in which two carbon atoms exchange more than one valence (p. 224). As the saturated compounds consist of the members of the first, or methane, series of hydrocarbons and their derivatives, so the unsaturated compounds are the remaining series of open chain hydrocarbons and their unsaturated derivatives (p. 229).

### HYDROCARBONS, ETHENE, OR OLEFIN SERIES.

The members of this series contain two atoms of carbon less than the corresponding terms of the methane series. They may be modified by addition, behaving as bivalent radicals, as well as by substitution. Their "Geneva" names terminate in **ene.**

**Ethene—Ethylene**—*Olefiant gas — Olefin —Elayl—Heavy carburetted hydrogen*—$CH_2:CH_2$—is formed by the dry distillation of fats, resins, wood, and coal, and is a valuable constituent of illuminating gas.

It is formed synthetically: (1) By heating a mixture of alcohol, $H_2SO_4$ and sand. In this reaction ethyl-sulfuric acid is formed and decomposed: $C_2H_5.HSO_4=H_2SO_4+CH_2:CH_2$. (2) By the action of caustic potash upon ethyl bromid: $CH_3.CH_2Br+KHO=KBr+H_2O+$

$CH_2:CH_2$. (3) By heating together acetylene and hydrogen, or by the action of nascent hydrogen upon copper acetylid: $CH{\vdots}CH+H_2=CH_2:CH_2$, or $C_2Cu_2+2H_2=CH_2:CH_2+2Cu$. (4) By heating methylene iodid with copper: $2CH_2I_2+2Cu=CH_2:CH_2+2CuI_2$. (5) By the action of sodium or of zinc upon ethylene chlorid or bromid: $CH_2Cl.CH_2Cl+Na_2=CH_2:CH_2+2NaCl$, or $CH_2Br.CH_2Br+Zn=CH_2:CH_2+ZnBr_2$.

It is a colorless gas, tasteless, has a faint odor of salt water, sparingly soluble in water. Its critical temperature is 13° (55.4° F.); its critical pressure 60 atmospheres. It boils at —105° (—157° F.).

It burns with luminous flame, and forms explosive mixtures with air. By long contact with a red-hot surface it is decomposed into acetylene, methane, ethane, a tarry product, and carbon. It unites with hydrogen to form ethane, $C_2H_6$; with oxygen it unites explosively on approach of flame, to form carbon dioxid and water. It combines with hydrobromic and hydriodic acids to form ethyl bromid, $C_2H_5Br$, and ethyl iodid, $C_2H_5I$. It combines with sulfuric acid to form ethyl-sulfuric acid: $CH_2:CH_2+H_2SO_4=C_2H_5.HSO_4$. Mixtures of ethene and chlorin explode, with copious deposition of carbon, on approach of flame. In diffuse daylight they unite slowly, with separation of an oily liquid, **ethylene chlorid**, or **dutch liquid**, $CH_2Cl.CH_2Cl$, to whose formation the name "olefiant gas" is due (p. 316). The same compound is formed when ethene is passed through a mixture of $MnO_2$, NaCl, $H_2SO_4$, and $H_2O$. When passed through alkaline solution of potassium permanganate, it is oxidized to oxalic acid and water: $2CH_2:CH_2+5O_2=2COOH.COOH+2H_2O$; or, by careful oxidation by dilute solution of the same agent, it forms ethene glycol: $2CH_2:CH_2+2H_2O+O_2=2CH_2OH.CH_2OH$ (p. 252).

When inhaled, diluted with air, ethene produces effects somewhat similar to those of nitrous oxid.

Two groupings of $(C_2H_4)''$ are possible, —$CH_2.CH_2$, —and $CH_3.CH=$, the former produced by the breaking of the double bond between the carbon atoms in ethene, the latter by double substitution in ethane. Compounds containing the grouping —$CH_2.CH_2$— are designated as **ethylene** or **ethene** compounds, e. g., **ethylene chlorid**, $ClCH_2.CH_2Cl$, b. p. 84°, those containing the grouping $CH_3.CH=$ are called **ethidene** or **ethylidene** compounds, e. g., **ethidene chlorid**, $CH_3.CHCl_2$, b. p. 58°.

**Homologues of Ethene.**—The superior homologues of ethene exist in coal gas and coal tar. They are formed by the methods 1 and 2, used for the preparation of ethene, but starting from the corresponding superior monoatomic alcohol. The lower terms are gaseous, the higher liquid at the ordinary temperature. They undergo reactions similar to those of ethene, and in addition, readily poly-

merize under the influence of sulfuric acid, zinc chlorid and other substances.

**Trimethyl-ethylene**—*Pentene*—*Amylene*—*Valerene*—$(CH_3)_2:C:CH.CH_3$—is a colorless, mobile liquid, boiling at 39° (102.2° F.), obtained by heating alcohol with a concentrated solution of zinc chlorid. It is used as an anæsthetic, and in the preparation of tertiary amylic alcohol (p. 251).

### ETHINE, OR ACETYLENE SERIES.

**Acetylene**—*Ethine*—$HC \vdots CH$—exists in coal gas, and is formed in the decomposition, by heat or otherwise, of many organic substances. It is formed: (1) By passing an electric arc in an atmosphere of hydrogen: $2C+H_2=CH \vdots CH$. This is the only known synthesis of a hydrocarbon directly from the elements. (2) By the action of water upon calcium carbid: $C_2Ca+2H_2O=HC \vdots CH+CaH_2O_2$. This method is used industrially for the preparation of acetylene for use as an illuminating gas. (3) By heating chloroform, bromoform or iodoform with sodium, copper, silver or zinc: $2CHCl_3+3Na_2=6NaCl+HC \vdots CH$. (4) By heating ethylene bromid with caustic potash. The reaction occurs in two phases, vinyl bromid being formed as an intermediate product: $CH_2Br.CH_2Br + KHO = CHBr:CH_2 + KBr + H_2O$, and $CHBr:CH_2+KHO=CH \vdots CH+KBr+H_2O$.

Acetylene is a colorless gas, rather soluble in water, having a peculiar, disagreeable odor, that which is observed when a Bunsen burner burns within the tube. It is liquefied by a pressure of 48 atmospheres at 0° (32° F.). It forms explosive mixtures with air or oxygen. In contact with a red-hot surface, and in absence of air, it polymerizes to benzene $3C_2H_2=C_6H_6$, an action which accounts for the presence of benzene in gas tar, and which is of great interest in connection with the relations between the open chain and the closed compounds (p. 378). Nascent hydrogen converts acetylene into ethene, $C_2H_4$, and then into ethane, $C_2H_6$. Under the influence of the electric discharge, it combines with nitrogen to form hydrocyanic acid: $C_2H_2+N_2=2CNH$. It combines with HCl and with HI to form ethidene chlorid, $CH_3.CHCl_2$, or iodid, $CH_3.CHI_2$. Mixed with chlorin it detonates violently in diffuse daylight. The hydrogen atoms of acetylene may be replaced by metals to form **acetylids**, or **carbids**. **Sodium** and **calcium acetylids** are stable at high temperatures, but are decomposed by water with formation of acetylene. **Silver** and **copper acetylids** are highly explosive when dry, and explosions which have occurred when illuminating gas was in contact with brass or copper were probably due to the formation of the latter. The formation of copper acety-

lid, which separates as a blood-red precipitate when acetylene is conducted through a solution of cuprous chlorid, is utilized as a test for the presence of acetylene. Acetylene mercuric chlorid, $C_2(HgCl)_2$, separates as a non-explosive, white precipitate when acetylene is passed through a solution of mercuric chlorid.

### DIOLEFIN AND SUPERIOR SERIES.

The **diolefins** are isomeric with the hydrocarbons of the acetylene series, containing two double linkages, in place of one triple linkage. Thus **allene**, or **allylene**, $CH_2{:}C{:}CH_2$, is isomeric with **propylene**, $CH{:}C.CH_3$. Higher series, p. 229.

**Olefin Terpenes—Terpenogens.**—While most essential oils and other aromatic substances are closed chain compounds, some ethereal oils contain or yield unsaturated, open chain hydrocarbons, alcohols, aldehydes or acids. Among the hydrocarbons are **myrcene**, and **anhydrogeraniol**, $C_{10}H_{16}$, the former obtained from bay-oil, the latter from oil of geranium. **Isoprene**, a product of distillation of caoutchouc, a liquid boiling at 37° (98.6° F.), is probably **methyl-divinyl**, $\begin{matrix}CH_3\\CH_2\end{matrix}\!\!>\!C.CH{:}CH_2$.

### UNSATURATED HALOGEN DERIVATIVES.

These cannot be formed directly, because addition products, such as ethylene chlorid, are formed in preference: $CH_2{:}CH_2+Cl_2=CH_2Cl.CH_2Cl$. But, by indirect methods, halogen derivatives of both olefins and acetylenes have been obtained, such as **vinyl chlorid**, $CH_2{:}CHCl$, and **vinyl bromid**, $CH_2{:}CHBr$. The propylene derivatives are $\alpha$ $CH_3.CH{:}CHCl$, $\beta$ $CH_3.CCl{:}CH_2$, or $\gamma$ $CH_2Cl.CH{:}CH_2$, according to the position of the substitution.

The $\gamma$ derivatives are the **allyl haloids**, corresponding to allylic alcohol. Of these, **allyl iodid**, $CH_2I.CH{:}CH_2$, is frequently used as a reagent. It is prepared by the action of hydriodic acid, or of iodin and phosphorus upon glycerol.

Corresponding to allyl iodid, but referable to propylene, are **propargyl iodid** and **chlorid**, $CH{:}C.CH_2I$ and $CH{:}C.CH_2Cl$, the latter produced by the action of phosphorus trichlorid upon **propargyl alcohol** (p. 372).

### UNSATURATED OXIDATION PRODUCTS OF UNSATURATED HYDROCARBONS

Like the paraffins, the olefins, acetylenes, diolefins, etc., yield alcohols, aldehydes, ketones, acids, oxids and esters (p. 237).

**Vinyl Alcohol**—$CH_2{:}CH.OH$—the simplest of the **olefin alcohols**,

is known only in a mercury compound. Although the radical, vinyl, $CH_2:CH$, is known in other compounds (see Neurin, p. 331), there is atomic transposition, with formation of aldehyde, $CH_2.CHO$, under conditions in which vinyl alcohol might be formed.

**Allyl Alcohol** — $CH_2:CH.CH_2OH$ — is formed: (1) By the action of sodium upon dichlorhydrin: $CH_2Cl.CHCl.CH_2OH + Na_2 = CH_2:CH.CH_2OH + 2NaCl$; (2) by heating allyl iodid with water: $CH_2:CH.CH_2I + H_2O = CH_2:CH.CH_2OH + HI$; (3) by reduction of acrolein by nascent hydrogen: $CH_2:CH.CHO + H_2 = CH_2:CH.CH_2OH$.

It is a colorless, mobile liquid, solidifies at —50° ( —58° F.), boils at 97° (206.6° F.), sp. gr. 0.8507 at 25° (77° F.), soluble in water, has an odor resembling the combined odors of alcohol and essence of mustard, burns with a luminous flame. It is isomeric with propylic aldehyde and with acetone. Oxidizing agents, such as silver oxid, convert it first into the corresponding aldehyde, **acrolein**, then into the acid, **acrylic acid**. It does not unite readily with hydrogen, but, in presence of nascent H, union takes place slowly, with formation of normal propyl alcohol. It forms products of addition with chlorin, bromin and iodin, similar to those derived from glycerol. Substitution compounds have also been obtained, such as **α bromallyl alcohol**, $CH_2:CBr.CH_2OH$, derived from **β dibromo-propylene**, $CH_2:CBr.CH_2Br$.

**Propargyl Alcohol** — $CH:C.CH_2OH$ — first of the **acetylene alcohols**, is formed by the action of caustic potash upon α bromallyl alcohol: $CH_2:CBr.CH_2OH + KHO = CH:C.CH_2OH + KBr + H_2O$.

**Rhodinol** — $C_{10}H_{20}O$ — b. p. 114°; **geraniol**, $C_{10}H_{18}O$, b. p. 120°; and **linalool**, $C_{10}H_{18}O$, b. p. 198, are **diolefin alcohols**, which are the chief constituents of the essential oils of rose, geranium, pelargonium, lavender, bergamot, etc.

**Acrylic Aldehyde — Acrolein** — $CH_2:CH.CHO$ — the first of the series of **olefin aldehydes**, is the substance which causes the disagreeable odor developed when fats or oils are overheated. It is formed: (1) By oxidation of allylic alcohol; (2) by distilling glycerol with strong $H_2SO_4$ or with $KHSO_4$: $CH_2OH.CHOH.CH_2OH = CH_2:CH.CHO + 2H_2O$.

Acrolein is a colorless liquid, having a pungent odor, and giving off a vapor which is intensely irritating; sp. gr. 0.841 at 20° (68 °F.), boils at 52° (125.6° F.), soluble in 2–3 parts of water. Oxidizing agents convert it into acrylic acid. Nascent hydrogen reduces it to allyl alcohol. It does not combine with alkaline bisulfites. It reduces ammoniacal silver nitrate solution as does acetic aldehyde. It suffers change even when kept in closed vessels, and deposits a white, flocculent material, which been called **disacryl**, while formic, acetic and acrylic acids are also produced.

**Croton Aldehyde** — $CH_3.CH:CH.CHO$. — By the action of diffuse daylight upon a mixture of acetic aldehyde, $H_2O$ and HCl, an oily liquid is slowly formed, which consists chiefly of **aldol**, or **β oxybutyraldehyde**, $CH_3.CHOH.CH_2.CHO$. This, when heated, is decomposed into croton aldehyde and water: $CH_3.CHOH.CH_2.CHO = CH_3.CH:CH.CHO + H_2O$.

Croton aldehyde is a colorless liquid; boils at 105° (221° F.), gives off highly irritating vapors; sp. gr. 1.033 at 0° (32° F.). It is reduced by nascent H to **crotonyl alcohol**, $CH_3.CH:CH.CH_2OH$.

**Propargyl Aldehyde** — $CH:C.CHO$ — is an **acetylene aldehyde**, a liquid, which boils at 59° (138.2° F.).

**Citronellal**, $C_{10}H_{18}O$, b. p. 104°, is an olefin aldehyde, existing in citronella and other essential oils. **Geranial**, $C_{10}H_{16}O$, b. p. 226°, is a **diolefin aldehyde** existing in lemon oil, and formed from geraniol.

**Mesityl Oxid**, $(CH_3)_2C:CH.CO.CH_3$, and **Phorone**, $(CH_3)_2C:CH.CO.CH:C(CH_3)_2$, are examples, respectively, of **olefin** and **diolefin ketones.** They are produced together by the action of dehydrating agents, such as $H_2SO_4$ and $ZnCl_2$, upon acetone. Mesityl oxid is a liquid, boiling at 130°, and having the odor of peppermint. Phorone is a solid, fusing at 28°, and boiling at 196°. **Methylheptenone**, $(CH_3)_2C:CH.CH_2.CH_2.CO.CH_3$, another olefin ketone, is a liquid having a penetrating odor, boiling at 173°, which exists in, or is produced from, many essential oils.

**Oleic Acids.**—The acids of this series are monocarboxylic acids derived from the olefins, and contain two atoms of hydrogen less than the corresponding terms of the acetic series. They are formed: (1) By oxidation of their corresponding alcohols or aldehydes. Thus allylic alcohol, $CH_2:CH.CH_2OH$, or acrolein, $CH_2:CH.CHO$, yield acrylic acid, $CH_2:CH.COOH$; (2) by the action of alcoholic KHO upon the monohalogen fatty acids. Thus β monobromo propionic acid yields acrylic acid: $CH_2Br.CH_2.COOH + KHO = CH_2:CH.COOH + KBr + H_2O$; (3) by dehydration of acids of the oxyacetic series. Thus ethylene lactic acid (β oxypropionic, p. 293) forms acrylic acid when heated: $CH_2OH.CH_2.COOH = CH_2:CH.COOH + H_2O$; (4) from the allyl haloids (p. 371), by conversion into cyanids and saponification. Thus crotonic acid is obtained from allyl iodid: $CH_2:CH.CH_2I + KCN = CH_2:CH.CH_2CN + KI$, and $CH_2:CH.CH_2CN + 2H_2O + HCl = CH_2:CH.CH_2.COOH + NH_4Cl$ (p. 278).

The oleic acids combine with the hydracids to form monohalogen fatty acids, the halogen assuming the position furthest removed from the carboxyl. Thus acrylic acid and hydriodic acid form β iodo propionic acid: $CH_2:CH.COOH + HI = CH_2I.CH_2.COOH$. Heated with caustic alkalies to 100°, they form oxyacids. Thus acrylic acid forms α lactic acid: $CH_2:CH.COOH + KHO = CH_3.CHOH.COOK$.

But, when fused with caustic alkalies, they are decomposed into fatty acids, with loss of H. Thus acrylic acid yields formic and acetic acids: $CH_2:CH.COOH+2KHO=H.COOK+CH_3.COOK+H_2$. The $\beta\gamma$ acids, i. e., those in which the double bond is between the $\beta$ and $\gamma$ positions, as in ethidene propionic acid, $CH_3.CH:CH.CH_2.COOH$, when heated with $H_2SO_4$ form lactones (p. 320).

**Acrylic Acid**—$CH_2:CH.COOH$—is best obtained by oxidizing acrolein with silver oxid. It is a liquid below 7° (44.6° F.), boils at 140° (284° F.), mixes with water, and has an odor like that of acetic acid.

**Crotonic Acids.**—Three crotonic acids are known, two of which are space isomerids (pp. 267, 375): **Ordinary crotonic acid,** $\begin{matrix}CH_3\\H\end{matrix}\!\!>\!C:C<\!\!\begin{matrix}COOH\\H\end{matrix}$, a crystalline solid, fusible at 72° (161.6° F.); **isocrotonic acid,** $\begin{matrix}H\\CH_3\end{matrix}\!\!>\!C:C<\!\!\begin{matrix}COOH\\H\end{matrix}$, a liquid boiling at 75° (167° F.), and **methacrylic acid,** $CH_2:C<\!\!\begin{matrix}COOH\\CH\end{matrix}$, a crystalline solid, f. p. 16°, b. p. 160°.

**Angelic Acid**—$\begin{matrix}H\\CH_3\end{matrix}\!\!>\!C:C<\!\!\begin{matrix}COOH\\CH_3\end{matrix}$—is a crystalline solid, f. p. 45°, b. p. 185°, having an aromatic odor, soluble in water, alcohol and ether. It exists free in angelica root, and, in its esters, in oil of cumin and in oil of anthemis. **Tiglic acid**—**Methyl-crotonic acid**—$CH_3.CH:C<\!\!\begin{matrix}COOH\\CH_3\end{matrix}$—isomeric with angelic acid, exists as a glycerid in croton oil, and, as its amyl ester, in oil of cumin. It is a crystalline solid, f. p. 65°, b. p. 198°.

**Hypogaeic Acid**—$C_{15}H_{29}.COOH$—accompanies arachic acid (p. 284) as its glycerid, in peanut oil. It is a crystalline solid, f. p. 33°, b. p. 236°.

**Oleic Acid**—$CH_3.(CH_2)_7.CH:CH.(CH_2)_7.COOH$—exists as its glyceric ester in fats and fixed oils, and is obtained in an impure form, on a large scale, as a by-product in the manufacture of stearin candles.

Pure oleic acid is a white, pearly, crystalline solid, fuses at 14° (57.2° F.), odorless, tasteless, soluble in alcohol and in ether, insoluble in water, sp. gr. 0.808 at 19° (66.2° F.), and neutral in reaction. Exposed to air, the liquid acid absorbs oxygen, and becomes yellow, rancid in taste and odor, acid in reaction, and incapable of solidification on cooling. Nitric acid oxidizes it, with formation of the lower fatty acids and **sebacic acid,** $C_{10}H_{18}O_4$. Heated to 200° (392° F.) with excess of caustic potash, it is split into palmitic and acetic acids: $C_{18}H_{34}O_2+2KHO=C_{16}H_{31}O_2K+C_2H_3O_2K+H_2$. The oleates of the alkaline metals are soft, soluble soaps; those of the earthy metals are insoluble in water. The action of iodin and of

bromin upon oleic acid is utilized in the analysis of fats and oils. At the ordinary temperature the fatty acids, including palmitic and stearic, are not affected by iodin, but the double bond in oleic acid is broken, and one molecule of oleic acid combines with two atoms of iodin. Under like conditions each molecule of linoleic acid (see below) takes up four atoms of iodin. The amount of iodin which a given weight of a fat or oil can combine with will increase with its tenure of oleic, or, particularly, of linoleic acid. "Hubl's **iodin number**" of a fat or oil is the quantity of iodin which 100 grams of the substance can take up under the conditions of the process, and is an important factor for its identification.

**Elaidic Acid** — $C_{17}H_{33}.COOH$ — is an isomere of oleic acid, produced from it by the action of nitrous acid. It is a crystalline solid, fusible at 51° (123.8° F.). Its formation is utilized to distinguish non-drying from drying oils (p. 318). The former, containing oleic acid, solidify when acted on by nitrous acid; the latter, containing linoleic acid, do not.

**Ricinoleic Acid**—$CH_3.(CH_2)_5.CHOH.CH_2.CH:CH.(CH_2)_7.COOH$ — is an unsaturated oxyacid, which exists as its glyceric ester in castor oil.

**Linoleic Acid** — $C_{17}H_{31}.COOH$ — is an unsaturated, pure acid, containing two atoms of hydrogen less than oleic acid. It exists as its glyceric ester in the drying oils, which dry and solidify on exposure to air.

**Propargylic Acid** —*Propiolic Acid* — $CH \vdots C.COOH$— corresponding to propargylic alcohol, is an example of an **acetylene monocarboxylic acid.** It is a liquid, having the odor of acetic acid. **Sorbic acid,** $CH_3.CH:CH.CH:CH.COOH$, is a **diolefin monocarboxylic acid,** derived from **parasorbic acid,** which is an unsaturated **oxyolefin acid** occurring in the berries of the mountain ash.

**Olefin dicarboxylic Acids.** — The acids of this series contain two atoms of hydrogen less than the corresponding acids of the oxalic series, and they consequently bear the same relation to those acids that the acids of the oleic series bear to those of the acetic series.

Esters of three acids having the composition $C_2H_2(COOH)_2$ are known. The free acid corresponding to one of these, **methylene malonic ester,** $CH_2:C\begin{matrix}COO(C_2H_5)\\COO(C_2H_5)\end{matrix}$, is not known. The other two, **fumaric** and **maleïc acids,** are "space isomerids" (p. 268). **Fumaric acid** is considered to have the axial symmetric structure: $\begin{matrix}H.C.COOH\\\|\\HOOC.C.H\end{matrix}$, because it does not yield an anhydrid, and because, on oxidation, it yields racemic acid, while maleïc acid has the plane symmetrical structure, because, owing to the closer proximity of the car-

boxyls, $\begin{matrix}H.C.COOH\\ \|\\ H.C.COOH\end{matrix}$, it readily forms an anhydrid, $\begin{matrix}H.C.CO\\ \|\\ H.C.CO\end{matrix}\!\!>\!O$, and because on oxidation it yields inactive, or meso-tartaric acid (see p. 267 and Fig. 31, ibid.).

Fumaric acid exists free in many plants, notably in Iceland moss. Fumaric and maleïc acids are readily converted one into the other by simple heating, and the two are produced together by the action of heat upon malic acid (p. 295), or by boiling solutions of monobromo-succinic acid (p. 288).

Fumaric acid crystallizes in small prisms, almost insoluble in cold water, which sublime at 200° (392° F.). Maleïc acid fuses at 130° (266° F.), and boils at 160° (320° F.). Both fumaric and maleïc acids are converted into succinic acid by nascent hydrogen.

Five unsaturated, open chain acids are known having the formula $C_3H_4(COOH)_2$, the next superior homologues of fumaric and maleïc acids. One of these, **ethidene malonic acid,** is only known in its esters $CH_3.CH:C\!<\!^{COO(C_2H_5)}_{COO(C_2H_5)}$. The structural formulæ of the others are:

| | | | |
|---|---|---|---|
| $\begin{matrix}H.C.COOH\\ \|\\ COOH.C(CH_3)\end{matrix}$ | $\begin{matrix}H.C.COOH\\ \|\\ (CH_3)C.COOH\end{matrix}$ | $\begin{matrix}CH_2:C.COOH\\ \|\\ CH_2.COOH\end{matrix}$ | $\begin{matrix}CH_2.COOH\\ \|\\ CH\\ \|\\ CH.COOH\end{matrix}$ |
| Mesaconic acid (Methyl-fumaric). | Citraconic acid (Methyl-maleïc). | Itaconic acid (Methylene succinic). | Glutaconic acid. |

**Mesaconic acid** is formed by heating citraconic or itaconic acid with water at 200° (392° F.). It is difficultly soluble in water, and fuses at 202° (395.6° F.). **Citraconic acid** is obtained from its anhydrid, $\begin{matrix}H.C.CO\\ \|\\ CH_3.C.CO\end{matrix}\!\!>\!O$, formed in the distillation of citric acid, by heating with water. Easily soluble in water, f. p. 80° (176° F.). **Itaconic acid** is similarly obtained from its anhydrid, a product of distillation of aconitic acid, f. p. 161° (320.2° F.). **Glutaconic acid** is formed by the action of barium hydroxid upon **coumalic acid,** an **oxydiolefin monocarboxylic acid,** having the composition $\begin{matrix}CH\!=\!\!=\!\!=\!C.COOH\\ |\qquad\quad |\\ O.CO.CH:CH.\end{matrix}$ It fuses at 132° (269.6° F.).

**Aconitic Acid**—$COOH.CH_2.C(COOH):CH.COOH$—is an **olefin tricarboxylic acid.** It exists as its Ca salt in a number of plants, including aconitum, equisetum, sugar-cane and beet-root. It is formed by heating citric acid (p. 297), either alone or with HCl or $H_2SO_4$. It is also obtained synthetically from a mixture of acetic and oxalic esters. It forms crystalline plates or prisms, soluble in water, alcohol, and ether, fuses at 191° (375.8° F.). Heat decom-

poses it into itaconic acid and $CO_2$. Nascent hydrogen reduces it to tricarballylic acid (p. 289).

**Allyl Oxid**—*Allylic ether*—$(CH_2:CH.CH_2)_2O$—is an example of the unsaturated ethers. It exists in small quantity in crude essence of garlic, and is formed by the action of allyl iodid upon sodium-allyl oxid. It is a colorless liquid, having the odor of garlic, insoluble in water, boiling at 82° (179.6° F.). Mixed ethers are also known, such as **propargyl ethyl ether**, $CH:C.CH_2.O.CH_2.CH_3$.

## UNSATURATED SULFUR AND NITROGEN COMPOUNDS.

**Allyl Sulfid**—$(CH_2:CH.CH_2)_2S$—corresponding to the oxid, is the principal constituent of volatile oil of garlic, obtained by distilling garlic with water. It is formed by the action of alcoholic solution of potassium sulfid upon allyl iodid. It is a colorless oil, lighter than water, soluble in alcohol and in ether, boils at 140° (280° F.).

**Allyl Isothiocyanate**—*Mustard oil*—$S:C:N.CH_2.CH:CH_2$—is the chief constituent of volatile oil of mustard, and of radish oil. It is prepared artificially by distilling allyl bromid or iodid with potassium or silver thiocyanate: $S:C:N.Ag+CH_2I.CH:CH_2=S:C:N.CH_2.CH:CH_2+AgI$. It does not exist preformed in the mustard seeds, but is produced by the decomposition of a glucosid, **potassium myronate** (p. 413), in the presence of water under the influence of an enzym, also contained in the seeds, called **myrosin**. The action takes place at 0° (32° F.), but not at temperatures above 40° (104° F.). The activity of myrosin is also impaired by the presence of acetic acid (vinegar). The pungent, rubefacient and vesicant actions of mustard are due to mustard oil.

Pure allyl isothiocyanate is a colorless oil, sp. gr., 1.015 at 20° (68° F.), boils at 150° (302° F.), has a penetrating, pungent odor, sparingly soluble in water, very soluble in alcohol and in ether. Exposed to air it gradually turns brownish-yellow, and deposits a resinoid material. Heated with HCl or with $H_2O$, it is decomposed into carbon dioxid, hydrogen sulfid and **allyl-amin**: $S:C:N.CH_2.CH:CH_2+2H_2O=CO_2+SH_2+NH_2.CH_2.CH:CH_2$.

Allyl-amin is the superior homologue of **vinyl-amin**, which is capable of uniting with sulfur dioxid and water to produce taurin or amido-isethionic acid (p. 366): $NH_2.CH:CH_2+SO_2+H_2O=NH_2.CH_2.CH_2.SO_3H$.

## CLOSED CHAIN COMPOUNDS—CYCLIC COMPOUNDS.

These compounds, which include many important natural products, and a practically unlimited number of synthetic compounds, differ from the members of the open chain series in that they contain a group of more than two atoms united together by exchange of valences in such a manner as to form a closed chain, or ring, or nucleus. If all the atoms so united are carbon atoms the substance belongs to the carbocyclic class; if an element other than carbon enters into the formation of the ring the substance is heterocyclic.

Some closed chain compounds are produced by the interaction of two open chain compounds, as in the formation of certain diamins (p. 330) and compound ureas (p. 351). Others, such as the lactids (p. 320), lactones (pp. 320, 362), and lactams (p. 362), are produced by internal reaction in an open chain molecule. But the principal method of formation of closed chain compounds is by polymerization. In some cases this takes place at comparatively low temperatures, as in the formation of trioxymethylene from formaldehyde (p. 257), and of the polymeric thioaldehydes and their sulfones (p. 322).

Among the instances of formation of cyclic from acyclic compounds there is one of polymerization at a high temperature which is of special interest as bearing upon the constitution of the cyclic compounds. The central figure of the carbocyclic compounds is benzene, $C_6H_6$, which is obtained principally from gas-tar. Coal gas contains acetylene, $C_2H_2$, and it is easy to conceive that one or two of the bonds uniting the two carbon atoms in acetylene may be loosened under the influence of heat, and that a molecule of benzene may be produced by fusion of three molecules of acetylene: $3C_2H_2 = C_6H_6$. The product so obtained is neither dipropargyl, $HC{:}C.CH_2.CH_2.C{:}CH$, nor dimethyl diacetylene, $H_3C.C{:}C.C{:}C.CH_3$ (p. 229), but another substance, the nature of whose substituted derivatives indicates that the six hydrogen atoms are of equal value, and therefore similarly attached to carbon atoms; and, there being three bisubstituted derivatives (p. 381), to at least three different carbon atoms. These conditions can only be fulfilled by a cyclic structure of the molecule of benzene and its derivatives (p. 380). Pyridin also, which has a prominence among the heterocyclic compounds corresponding to that of benzene among the carbocyclic, has been obtained from acetylene and hydrocyanic acid by a fusion very similar to that by which acetylene alone forms benzene: $2C_2H_2 + HCN = C_5H_5N$. It is also formed by the action of heat upon substances containing nitrogen as well as carbon (p. 459)

# CARBOCYCLIC COMPOUNDS.

Carbocyclic compounds are known containing from three to seven carbon atoms in a ring. Compounds are also known containing a much larger number of carbon atoms, but these are formed by fusion or union of two or more rings of six carbon atoms or less, or by the attachment of an open chain grouping upon a closed chain one (p. 438). The hexacarbocyclic compounds are far more numerous and important than the others.

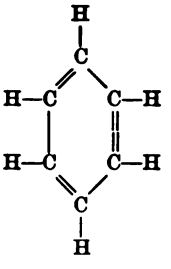
The mononuclear carbocyclic hydrocarbons have algebraic formulæ varying from $C_nH_{2n}$ to $C_nH_{2n-6}$, and are isomeric with the unsaturated open chain hydrocarbons (p. 229). Those of the series $C_nH_{2n}$ are known as **polymethylenes**, being considered as formed by the union of a number of methylene groups, $CH_2$. Thus **hexahydrobenzene** is **hexamethylene**, $CH_2\langle^{CH_2.CH_2}_{CH_2.CH_2}\rangle CH_2$. But the chemical relations of the polymethylenes to the saturated hydrocarbons is closer than that to their isomeres, the olefins, because, containing no double linkages, they cannot be modified by addition without disruption of the ring. So long as the cyclic formation is maintained, the polymethylenes are saturated compounds, as are the paraffins. For this reason their "Geneva" names are the same as those of the paraffins of like carbon content, to which is prefixed the syllable "**cyclo**," and they are known generically as **cycloparaffins**; or the symbol R is used in place of the syllable "cyclo." The hydrocarbons of the series $C_nH_{2n-2}$, isomeric with the acetylenes and diolefins, are referable to the latter, not to the former, as they cannot contain a triple linkage in the ring. But, containing only one double linkage, they are more closely related to the olefins. Therefore **tetrahydrobenzene**, $CH\langle^{CH.CH_2}_{CH_2.CH_2}\rangle CH_2$, isomeric with hexadiëne, $CH_2{:}CH.CH_2.CH_2.CH{:}CH_2$, containing but one double linkage, is **cyclo-hexene**, or **R-hexene**. Similarly **dihydrobenzene**, $CH\langle^{CH_2.CH_2}_{CH.CH}\rangle CH$, is a **cyclodiolefin: R-hexadiëne**; and benzene a **cyclotriolefin: R-hexatriëne.**

The cycloparaffins are formed by the action of sodium upon the dibromoparaffins. Thus trimethylene is obtained from trimethylene bromid: $CH_2Br.CH_2.CH_2Br+Na_2=CH_2\langle^{CH_2}_{CH_2}+2NaBr.$

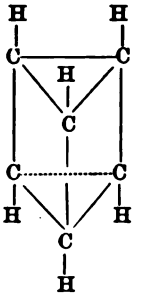
**Tri-, tetra-, penta-,** and **hepta-carbocyclic hydrocarbons,** and their numerous derivatives, notably acids and ketones, are known. They are not as yet, however, of medical interest, except that certain tetra-, and penta-compounds are among the decomposition products of certain alkaloids.

## HEXACARBOCYCLIC COMPOUNDS — AROMATIC SUBSTANCES.

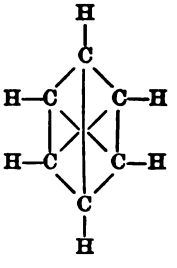
These compounds, which are very numerous and important, all contain a group of six carbon atoms, to which are attached six, eight, ten or twelve univalents, or their equivalent. As the simplest representative of the class is benzene, $C_6H_6$, and as all of these bodies may be derived from benzene, directly or indirectly, and yield that hydrocarbon on decomposition, *the aromatic substances may be considered as derivatives of benzene.* This being the case, the constitution of benzene itself is of great importance, and has been the subject of much study. Several schematic representations of the structure of the benzene molecule have been suggested, the most demonstrative of which are the hexagonal form of Kekulé, the prismatic form of Ladenburg, and the diagonal form of Claus:



Hexagonal.



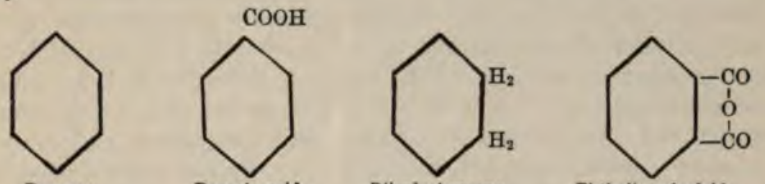
Prismatic.



Diagonal.

In the hexagonal formula the carbon atoms exchange one and two valences alternately, each being attached to two others; in the prismatic form each carbon atom is attached to three others by single valences; and in the diagonal form the hexagon is retained, but, in place of double linkages, a central linkage between all the carbon atoms is substituted. All of these formulæ represent the equivalence of the carbon atoms, and the constitution of isomeres equally well (see below). The prismatic formula cannot be modified to represent a constitution of the additive derivatives of benzene, such as dihydrobenzene, $CH\langle\begin{matrix}CH_2.CH_2\\CH.CH\end{matrix}\rangle CH$, and tetrahydrobenzene, $CH\langle\begin{matrix}CH_2.CH_2\\CH.CH_2\end{matrix}\rangle CH_2$. Neither the prismatic nor the diagonal formula admits double linkages between carbon atoms in the ring. That these exist is shown, however, by the formation of the additive products mentioned, by the formation of anhydrids from ortho-derivatives only (see below), and by certain physical properties. Moreover, the hexagonal formula ac-

cords well with the tetrahedral representation of the valences of the carbon atom (p. 267), the six tetrahedra being alternately united by edges and apexes in benzene, and by apexes in hexahydrobenzene. For these (and other) reasons, chemists have very generally adopted the hexagonal expression, although it still leaves something to be desired. The figure of a hexagon is used in chemical writings to represent the benzene ring. If used alone it represents a molecule of benzene, $C_6H_6$; and to represent the products of substitution the symbols of the substituted group are written in the proper position, thus :




Benzene. Benzoic acid. Dihydrobenzene. Phthalic anhydrid.

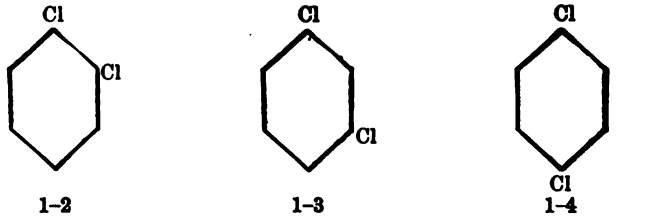
**Isomery of Benzene Substitution Products.**—(1) *The six atoms of hydrogen in benzene are of equal value.* There exists but one mono-substituted derivative of benzene containing any given univalent: one chlorobenzene, $C_6H_5Cl$, one nitro-benzene, $C_6H_5(NO_2)$, one amido-benzene, $C_6H_5(NH_2)$, one benzoic acid, $C_6H_5.COOH$, etc. Therefore, benzene is symmetrical in structure, and its hydrogen atoms equal each other in value, as do those of methane, while those of pyridin (p. 454) are not all of like value.

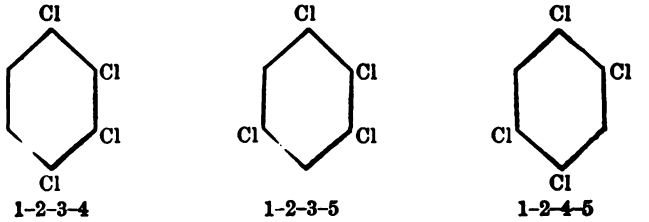
2. *Any hydrogen atom selected in the benzene ring is symmetrically placed in reference to two pairs of hydrogen atoms, and to the sixth hydrogen atom individually.* With all di-, tri-, and tetra-substituted derivatives of benzene, containing like substituted univalents, there are three isomeres. Three dichloro-, three trichloro-, and three tetrachloro-benzenes, etc., and in no instance are more than three known. There is but one explanation of the facts mentioned above, namely, that the different bi-, tri-, and tetra-derivatives are produced by differences in the relative positions of the substituted groups, by differences in " orientation," as among the aliphatic compounds, the several oxyacids are "place isomeres" of each other (p. 290).

The hexagonal formula of benzene is very convenient for showing the structure of the several isomeres. For this purpose the carbon atoms are numbered, beginning, for convenience, at the top and proceeding clockwise.

It has been demonstrated that in some of the bisubstituted derivatives the two substituted groups are attached to **adjacent** carbon atoms, i. e., to 1-2, 2-3, 3-4, 4-5, 5-6, or 6-1.

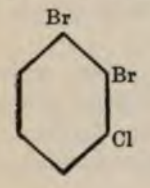
Clearly for each carbon atom there is a pair of adjacent positions, as 1-2 and 1-6, 2-1 and 2-3, etc., which are equivalent to each other.* In other bisubstituted derivatives it may be shown that the two substituted groups are attached to carbon atoms, separated from each other by one carbon atom on one side and by three on the other, an arrangement which renders the hexagon unsymmetrical. Such positions are 1-3, 2-4, 3-5, 4-6, 5-1, and 6-2. Or, for each carbon atom there is a pair of equivalent unsymmetrical positions, as 1-3 and 1-5, etc. There remains but one other arrangement possible, the symmetrical, or diagonal, 1-4, 2-5, 3-6. With the tri- and tetra-substituted derivatives there are also three possible arrangements: the adjacent, vicinal, or consecutive, as 1-2-3, 2-3-4; 1-2-3-4, or 2-3-4-5; the unsymmetrical, as 1-2-4, 3-4-6; 1-2-3-5, or 3-4-5-1; and the symmetrical, as 1-3-5, 2-4-6; 1-2-4-5, or 3-4-6-1. Compounds in which the substitution is adjacent are designated as ortho-compounds (ὀρθός=straight), or, in writing, by the abbreviation o-, or by the figures 1-2, etc. Thus $C_6H_4(OH)_{2(1-2)}$, o-diphenol. Unsymmetrical compounds are designated as meta-compounds (μετά-after), or, abbreviated, m-, or by the figures, 1-3, etc.: e. g., $C_6H_3(Br)_{3(1-3-5)}$, m-tribromobenzene. Symmetrical compounds are designated as para-compounds (παρά-beside), abbreviated p-, or 1-4, etc.: e. g., $C_6H_2(NH_2)_{4(1-3-4-5)}$, p-tetraamido-benzene. Or, to illustrate by the formulæ of the di- and tetra-chlorobenzenes:



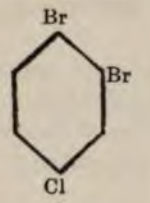




*NOTE.—The principal objection to the hexagonal formula of benzene (and stated by Kekulé himself) is that these two positions are not entirely equivalent, as in the position 1-2 the grouping is=C—C=, while in 1-6 it is—C=C—, and that consequently there should be two ortho derivatives, while but one is known. The student is referred to more extended works for a discussion of this subject.

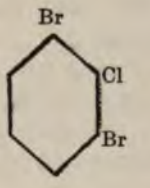
In the bisubstituted derivatives it is immaterial whether the two substituted groups are of the same kind or different. But when, in a trisubstituted derivative, the substituted groups are not the same in kind, the number of possible isomeres is increased. Thus there are six possible chloro-dibromobenzenes (formulæ 1 to 6 below), of which two (1 and 2) are derived from orthodibromobenzene, $C_6H_4:Br_{2(1,2)}$ three (3, 4, and 5) from metadibromobenzene, $C_6H_5:Br_{2(1,3)}$, and one (6) from paradibromobenzene, $C_6H_4:Br_{2(1,4)}$. The number of possible trisubstituted derivatives is increased to ten when all three substituted groups are of different kind.



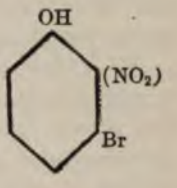

1
Orthodibromo-metachloro.



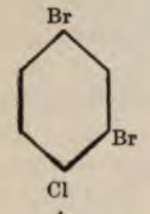

2
Orthodibromo-parachloro.



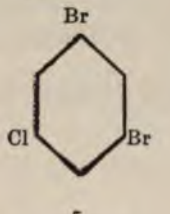

3
Metadibromo-orthochloro.



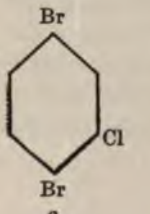

7



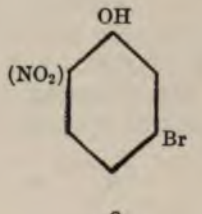

4
Metadibromo-parachloro.




5
Metadibromo-allometachloro.




6
Paradibromo-metachloro.




8

In naming these derivatives, the characterizing group of the parent substance is given the position 1 in the hexagon, the prefix "**ortho**" is applied to the name of the group occupying one of the ortho positions 2 and 6, "**meta**" to that occupying one of the meta positions 3 and 5, and "**para**" to that occupying the para position 4. Thus the substance having the formula 7 above is **orthonitro-para-bromo-phenol.** But another substance is known, not identical with this, having the formula 8 above, in which the nitro group occupies the second ortho position, 6. To distinguish substances such as these, the designation "**allortho**" is given to the position 6, and the designation "**allometa**" to the position 5. Thus the substance having the formula 8 is **metabromo-allorthonitro-phenol.** When formulæ are used the numerals corresponding to the position of substitution, enclosed in brackets, are placed after the symbols. Thus 7 is written: $C_6H_3(OH)(NO_2)_{[2]}\,Br_{[3]}$, and 8: $C_6H_3(OH)Br_{[3]}\,(NO_2)_{[6]}$.

**Classification of Aromatic Substances.**—The benzene derivatives may be classified into five classes:

A. Compounds containing a single benzene nucleus, unmodified except by substitution for hydrogen. Monobenzenic compounds. Includes benzene and its homologues, and the phenols, alcohols, acids, etc., derived from them.

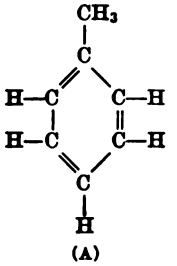
B. Compounds containing a single benzene nucleus in which one (or more) of the double bonds has been converted into a single one, thus adding two, four, or six valences to the carbon ring. Monohydrobenzenic compounds. Includes the cyclohexadiënes, cyclohexenes, and cyclohexanes (p. 379), and their derivatives, among which are the terpenes and camphors.

C. Compounds containing two (or more) benzene nuclei, or benzene and pentacarbocyclic rings, fused together, and having two carbon atoms in common. Includes indene, fluorene, naphthalene, anthracene, and phenanthrene and their derivatives. Compounds with condensed nuclei.

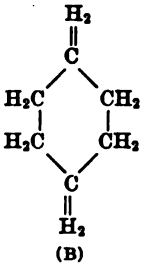
D. Compounds containing two (or more) benzene rings, directly united by loss of two H atoms. Diphenyl and its derivatives.

E. Compounds containing two (or more) benzene nuclei, united by aliphatic groups. Includes di- and polyphenyl paraffins, olefins and acetylenes and their derivatives.

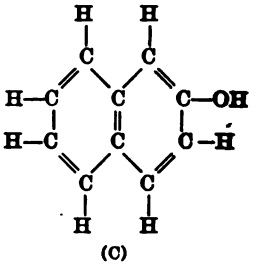
The following formulæ will serve to indicate the differences in constitution of the several classes:



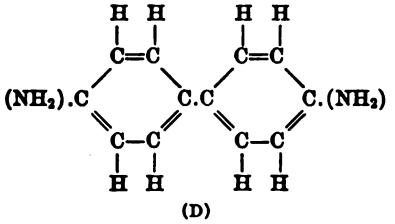
(A)
Methyl-benzene.



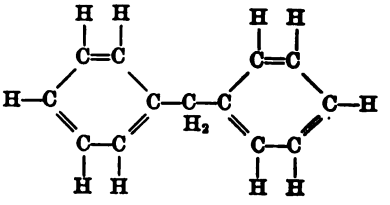
(B)
Hexahydrobenzene.



(C)
β Naphthol.



(D)
ps—Diamido-diphenyl.



(E)
Diphenyl-methane.

## A. MONOBENZENIC COMPOUNDS.

### HYDROCARBONS.

**Benzene** — *Benzol* — $C_6H_6$ — (not to be confounded with *benzine*, a mixture of hydrocarbons of the series $C_nH_{2n+2}$, obtained from petroleum — p. 232) does not exist in nature. It is obtained, pure, by decomposing benzoic acid by heating with slaked lime: $C_6H_5.COOH + CaH_2O_2 = CaCO_3 + C_6H_6 + H_2O$. It is produced in the distillation of coal, and exists in coal tar, from which it is obtained for use in the arts.

Coal tar, or gas tar, is a very complex mixture, containing forty or fifty substances — hydrocarbons, phenols and bases — and is the crude material from which many important substances are obtained. In working it, it is first distilled, four fractions being collected: (1) *Light oil*, distilling below 150° (302° F.); (2) *carbolic oil*, or *middle oil*, distilling below 230° (446° F.). Contains phenols and naphthalene. (3) *Heavy oil*, or *creasote oil*, distilling below 270° (518° F.). Furnishes naphthalene. (4) *Green oil*, or *anthracene oil*, distilling above 270°. Contains anthracene and other solid hydrocarbons. The residue in the still is pitch. The light oil contains benzene, toluene and xylene, with some thiophene, phenols, pyridin, and heavy oils. It is further purified to yield various grades of commercial "*benzol*," the best of which contains about 70 per cent. of benzene, and 24 per cent. of toluene, with some xylene, cumene and thiophene.

Pure benzene is a colorless liquid, having an ethereal odor, crystallizing at 5.4° (41.7° F.), boiling at 80.5° (176.9° F.), sp. gr. 0.86 at 15° (59° F.), immiscible with water, mixing with alcohol and ether. It dissolves I, S, P, resins, caoutchouc, guttapercha, fats and many alkaloids. It is inflammable, and burns with a smoky flame.

Benzene unites directly with Cl or Br to form products of addition or of substitution. Free Cl acts only slowly upon benzene alone, but the action is much accelerated by the presence of certain chlorids, particularly $Fe_2Cl_6$. The corresponding I derivatives can only be obtained indirectly. Sulfuric acid combines with it to form **benzene sulfonic acid**, $C_6H_5.SO_3H$. Nitric acid converts it into nitro-benzene, $C_6H_5.NO_2$, or, if fuming $HNO_3$ is used and the mixture boiled, into a mixture of the three dinitro-benzenes, $C_6H_4(NO_2)_2$. It is reduced to hexahydrobenzene by hydriodic acid.

**Homologues of Benzene.**— These may be considered as alkyl-benzenes, formed by the substitution of alkyl groups for an equivalent number of hydrogen atoms in benzene. The usual general method

of their formation indicates the constitution: they are obtained by treating a mixture of bromobenzene, ether, and the bromid or iodid of the corresponding alcoholic radical with sodium. Thus monobromo-benzene and methyl bromid yield methyl-benzene, or toluene: $C_6H_5Br + CH_3Br + Na_2 = 2NaBr + C_6H_5.CH_3$. They are also formed by the action of the alkyl chlorids upon the inferior homologues in presence of $Al_2Cl_6$, or of $ZnCl_2$, or $Fe_2Cl_6$. Thus benzene and methyl chlorid form toluene: $C_6H_6 + CH_3Cl = C_6H_6.CH_3 + HCl$. This is a general method frequently used for the introduction of alkyls into aromatic compounds, and probably depends upon the formation of intermediate organo-metallic compounds (p. 325). There are numerous other methods for their production. The superior homologues of benzene include many isomeres. Thus there are:

| | |
|---|---|
| 1-$C_7H_8$, i. e., | $C_6H_5(CH_3)$-Methyl-benzene, |
| 4-$C_8H_{10}$, i. e., three | $C_6H_4(CH_3)_2$-o-, m-, and p-Dimethyl-benzenes, |
| | $C_6H_5(C_2H_5)$-Ethyl-benzene, |
| 8-$C_9H_{12}$, i. e., three | $C_6H_3(CH_3)_3$-o-, m-, and p-Trimethyl-benzenes, |
| three | $C_6H_4(CH_3)(C_2H_5)$-o-, m-, and p-Methyl-ethyl benzenes, |
| | $C_6H_5(C_3H_7)$-Propyl-benzene, |
| | $C_6H_5(C_3H_7)$-Isopropyl-benzene, |
| 19-$C_{10}H_{14}$, i.e., three | $C_6H_2(CH_3)_4$-o-, m-, and p-Tetramethyl benzenes, |
| three | $C_6H_4(C_2H_5)_2$-o-, m-, and p-Diethyl-benzenes, |
| three | $C_6H_3(CH_3)_2(C_2H_5)$-o-, m-, and p-Dimethylethyl-benzenes, |
| three | $C_6H_4(CH_3)(C_3H_7)$-o-, m-, and p-Methylpropyl-benzenes, |
| three | $C_6H_4(CH_3)(C_3H_7)$-o-, m-, and p-Methylisopropyl-benzenes, |
| four | $C_6H_5(C_4H_9)$-Butyl-benzenes. |

The homologues of benzene are acted upon by reagents in the same manner as benzene itself. In addition, the lateral chain may be acted upon. Benzene is not acted upon notably by oxidizing agents unless they be sufficiently powerful to disrupt the molecule. But oxidants such as dilute nitric acid, or the chromic mixture, oxidize the lateral chain in the homologues of benzene, with formation of carboxylic acids. Thus methyl-benzene, $C_6H_5.CH_3$, yields benzoic acid, $C_6H_5.COOH$.

**Toluene—Toluol—Methyl-benzene**—$C_6H_5.CH_3$—exists in the products of distillation of coal, wood, etc., and is a constituent of commercial benzene. It is formed synthetically by the general methods given above; or may be obtained pure by decomposition of one of the toluic acids by lime.

It is a colorless liquid, boils at 110.3° (230.5° F.), does not solidify at —20° (—4° F.), sp. gr. 0.872 at 15° (59° F.), does not mix with water, but mixes with alcohol, ether and carbon disulfid.

**Xylenes—Xylols**—$C_8H_{10}$.—Four isomeres are possible and are known: ethyl-benzene, $C_6H_5.C_2H_5$—and ortho- (1—2), meta- (1—3),

and **para-** (1—4), **dimethyl-benzenes**, $C_6H_4(CH_3)_2$. **Ethylbenzene** is a colorless oil, boiling at 134° (273.2° F.), obtained by fractional distillation of animal oil. The three **dimethyl benzenes** exist in coal tar and in the commercial xylene, which boils at 139° (282.2° F.), 70% consisting of metaxylene, and paraxylene being present in very small amount. **Mesitylene,** formed by distilling acetone or allylene with $H_2SO_4$ is p-trimethylbenzene. **Cymene**, a liquid having a pleasant odor, present in several ethereal oils, is p-methylisopropyl-benzene. It is formed by the action of methyl iodid upon p-bromo isopropyl benzene in presence of sodium.

### MONOBENZENIC HYDROCARBONS WITH UNSATURATED LATERAL CHAINS.

These are similar in constitution to the homologues of benzene, except that the lateral chains are olefins or acetylenes, in place of paraffins.

**Styrolene — Cinnamene — Ethylenebenzene — Phenylethene** — $C_6H_5.CH:CH_2$—exists ready formed in essential oil of styrax. It is also formed by decomposition of cinnamic acid (p. 402), or, synthetically, by the action of a red heat upon pure acetylene, a mixture of acetylene and benzene, or a mixture of benzene and ethylene. It is a colorless liquid, has a penetrating odor, recalling those of benzene and naphthalene, and a peppery taste; boils at 143° (289.4° F.); soluble in all proportions in alcohol and water; neutral in reaction.

**Phenyl-acetylene — Acetenyl-benzene** — $C_6H_5.C:CH$—is formed by heating acetophenone chlorid with KHO in alcoholic solution. It is a colorless liquid, of an aromatic odor, boils at 140° (284° F.).

### HALOID DERIVATIVES.

By the substitution of atoms of Cl, Br and I for the hydrogen of the principal and lateral chains in benzene and its superior homologues, a great number of subtances are obtained, many of them forming isomeric groups.

The chlorin derivatives of benzene are:

**Monochloro-benzene**—$C_6H_5Cl$—liquid; boils at 132° (269.6° F.); sp. gr. 1.128 at 0°; obtained by the action of Cl upon $C_6H_6$ in the cold, in the presence of a little I.

**Orthodichloro-benzene**—1—2—liquid; boils at 179° (354.2° F.); sp. gr. 1.328 at 0°; obtained by the action of Cl on $C_6H_6$.

**Metadichloro-benzene**—1—3—liquid; boils at 172° (341.6° F.); sp. gr. 1.307 at 0°; obtainable indirectly.

**Paradichloro-benzene**—1—4—crystalline; fuses at 56.4° (133.5°

F.); boils at 170° (343.4° F.); is the principal product of the action of Cl on $C_6H_6$ in presence of I.

**Metatrichloro-benzene**—1—2—4—crystals; fuses at 17° (62.6° F.); boils at 213° (415.4° F.).

**Paratrichloro-benzene**—1—3—5—crystals; fuses at 63.4° (146.1° F.); boils at 208° (406.4° F.).

**Tetrachloro-benzene**—1—2—3—5—crystals; fuses at 50° (122° F.); boils at 246° (474.8° F.).

**Tetrachloro-benzene**—1—2—4—5—crystals; fuses at 137° (278.6° F.); boils between 243°–246° (469.4°–474.8° F.).

**Benzyl chlorid**—$C_6H_5.CH_2Cl$—is an example of the substitution of a halogen in the lateral chain of a superior homologue of benzene. It is obtained by the action of chlorin upon boiling toluene; or of $PCl_5$ on benzylic alcohol. It is a colorless liquid, boils at 176° (348.8° F.), and gives off pungent vapors which excite the lachrymal secretion. It is readily oxidized to benzoic aldehyde or benzoic acid, and serves for the introduction of the radical benzyl into other molecules. The radical of benzylic alcohol ($C_6H_5.CH_2$), (p. 397) is called **benzyl**; that of benzoic acid, ($C_6H_5.CO$), **benzoyl** (p. 401).

## BENZENIC OXYGEN COMPOUNDS.

The derivatives of benzene containing oxygen include, besides **alcohols, aldehydes, ketones, acids, ethers,** and **anhydrids,** corresponding to those of the open chain series, a class of **hydroxids,** the **phenols,** of which there are no aliphatic prototypes.

## PHENOLS.

In the phenols the hydroxyl is substituted for the hydrogen of the benzene ring, while in the alcohols the substitution occurs in a lateral chain. Thus phenol is $C_6H_5.OH$; benzylic alcohol, $C_6H_5.CH_2OH$. All six of the hydrogen atoms of benzene may be thus replaced to form **monohydric phenols, dihydric phenols,** etc.

In their properties the phenols differ from the alcohols by more nearly approaching the character of the acids. On oxidation they do not furnish aldehydes or acids; they do not divide into water and hydrocarbon under the influence of dehydrating agents; they do not react with acids to form esters; they combine directly with Cl and Br to form products of substitution; they form with the metallic elements compounds more stable than similar compounds of the true alcohols.

The phenols occur in nature in small quantities only; some in the vegetable world, and some in combination as ester sulfuric acids in

the urine. They are mostly products of distillation of wood, coal, etc.

### MONOATOMIC—MONOHYDRIC PHENOLS.

The monoatomic phenols are produced: (1) by fusing the corresponding sulfonic acids with caustic alkali: $C_6H_5.SO_3K+KHO=C_6H_5.OH+K_2SO_3$; (2) by decomposition of the diazo-compounds (p. 427) by boiling with water: $C_6H_5.N:N.HSO_4+H_2O=C_6H_5.OH+N_2+H_2SO_4$; (3) the higher phenols are produced by heating phenol with $ZnCl_2$ and the alcohols, a phenolic ether being also formed. Thus phenol and methylic alcohol yield cresol and methyl-phenyl ether: $2C_6H_5.OH+2H.CH_2OH=C_6H_4.OH.CH_3+C_6H_5.O.CH_3+2H_2O$.

The phenols are reduced to hydrocarbons by heating with zinc dust. Their ring-hydrogen is readily replaceable by other elements or groups to form haloid, nitro, amido derivatives, etc. Their hydroxyl hydrogen is also readily replaceable by alkyls to produce ethers, by Na, K, and Ca to produce phenates, and by acidyls to produce phenyl esters (p. 391). The phenols combine with the diazo compounds to produce azo- and diazo dyes, and with phthalic acid to produce phthaleïns.

**Phenol—Benzophenol**—*Phenyl hydroxid*—*Phenic acid*—**Carbolic acid**—$C_6H_5.OH$—exists in considerable quantity in coal- and wood-tar, and in small quantity in castoreum and, in combination, in the urine. It is produced in the intestine.

It is formed: (1) by fusing sodium-phenyl sulfid with excess of alkali: $C_6H_5.NaS+NaHO=C_6H_5.OH+Na_2S$; (2) by heating phenyl iodid and potassium hydroxid at 320° (608° F.): $C_6H_5I+KHO=C_6H_5.OH+KI$; (3) by heating together salicylic acid and quicklime; $C_6H_4.OH.COOH+CaH_2O_2=C_6H_5.OH+CaCO_3+H_2O$; (4) by total synthesis from acetylene, through benzene (p. 378), and its sulfonic acid; (5) by decomposition of the phenylic esters by alkalies. Thus salol yields phenol and salicylic acid: $C_6H_4.OH.COO(C_6H_5)+KHO=C_6H_5.OH+C_6H_4.OH.COOK$; (6) by dry distillation of benzoin. "Synthetic phenol," prepared by method (4), is now manufactured. "Carbolic acid" is obtained from the "middle oil" of gas tar (p. 385). It is purified by conversion into potassium phenate, $C_6H_5.OK$, which is crystallized, decomposed by HCl, and the liberated phenol recrystallized and distilled.

Phenol is extensively used, not only as an antiseptic, but also in the manufacture of numerous derivatives, including medicinal compounds, dyes and explosives.

Phenol crystallizes in long, colorless needles, fuses at 43° (109.4° F.), boils at 183° (361.4° F.), sp. gr. 1.084 at 0° (32° F.), has a characteristic odor, and an acrid, burning taste, soluble in 15 parts

of water at 20° (68° F.), very soluble in alcohol and in ether, neutral in reaction. It may be distilled without decomposition.

Its vapor is reduced to benzene by heating with Zn. It combines with $H_2SO_4$ to form o-, and p-phenol sulfonic acids. With $HNO_3$ it forms 2-4-6-trinitrophenol. Heated with sulfuric and oxalic or arsenic acid, it yields several triphenyl-methane dyes, among which are corallin, rosolic acid, peonin, azulin, aurin, and phenicin.

**Analytical Characters**—(1) Its peculiar odor. (2) Mix with one quarter volume of $NH_4HO$; add two drops of sodium hypochlorite solution, and warm: a blue or green color. Add HCl to acid reaction: turns red. (3) Add two drops of the liquid to a little HCl, and then a drop of $HNO_3$: a purple red color. (4) Boil with $HNO_3$ so long as red fumes are given off, neutralize with KHO: a yellow, crystalline precipitate. (5) Float the liquid on $H_2SO_4$, add powdered $KNO_3$: a violet color. (6) With solution of $FeSO_4$: a lilac color. (7) Add excess of bromin water: a yellowish-white precipitate. This compound, tribromophenol, $C_6H_2Br_3OH$, is the form in which phenol is quantitatively determined; 100 parts of it correspond to 29.8 parts of phenol. (8) Moisten a pine shaving with the liquid, then with HCl, to which a trace of $KClO_3$ has been added immediately before use, and expose to sunlight: a fine blue color. The test should be tried also with a solution of phenol, and with the acid alone, as only certain varieties of pine are suitable. (Pine-shaving reaction. See also Pyrrole.)

**Toxicology.**—Carbolic acid is an active poison and corrosive. It has caused death in a dose of 1.5 gram. The average duration of fatal cases is 2–8 hours. Death may occur in 3–5 minutes from collapse. It causes a burning sensation, soon followed by intense pain and cauterization of all parts with which it comes in contact. The stain which it produces is at first white, after a few minutes; later it turns darker and, when the eschar separates, a brown stain remains, which persists for many days. Vomiting usually occurs, the vomited matters, as well as the breath, having the odor of carbolic acid. The patient soon becomes unconscious, and death is from collapse or in coma. The urine, normal in color when first voided, soon becomes olive-green, brown, or even black in color, The treatment consists in administration of albumen, saccharated lime, sodium sulfate, or strong alcohol, followed by lavage.

**Phenates.**—*Carbolates.*—The oxhydryl hydrogen of phenol is replaceable by certain metals and by alkyls to form phenates and phenyl ethers. When phenol and KHO are heated together, **potassium phenate,** $C_6H_5OK$, is formed. This, when treated in alcoholic solution with $HgCl_2$, produces **mercuric phenate,** $(C_6H_5O)_2Hg$, a yellow, crystalline solid which has been used in medicine.

The **phenyl ethers** are formed by heating the metallic phenates with the alkyl haloids: $C_6H_5.O.K+CH_3I=C_6H_5.O.CH_3+KI$, as the aliphatic ethers are produced from the alkyl haloids and the metallic alcoholates (p. 299). They are to be regarded as simple ethers, rather than as phenates (see also sodium ethylate, p. 244, and Glucosids, p. 409). The **phenyl esters**, on the other hand, are formed by the action of the acidyl chlorids upon the phenols, or upon their metallic derivatives: $C_6H_5.OH+CH_3.COCl=CH_3.CO_2.C_6H_5+HCl$, or, $C_6H_5.OK+CH_3.COCl=CH_3.CO_2.C_6H_5+KCl$, as the aliphatic esters are formed by the action of acidyl haloids upon the alcohols or upon the alcoholates (p. 312).

**Methyl-phenyl Ether — Anisol** — $C_6H_5.OCH_3$ — is a colorless, thin liquid, boils at 152° (305.6° F.) without decomposition. Sulfuric acid dissolves it, with formation of methyl-phenol sulfonic acid.

**Ethyl-phenyl Ether—Phenetol**—$C_6H_5.OC_2H_5$—is a colorless liquid, having an aromatic odor. It boils at 172° (341.6° F.).

Anisol and phenetol serve as the starting-points for the production of the **anisidins** and **phenetidins** (p. 423).

**Cresols—Cresylols—Cresylic acids—Benzylic or cresylic phenols**—$C_6H_4\langle^{CH_3}_{OH}$—108.—Of the three possible compounds, two, the para and ortho, accompany phenol in coal-tar, from which they may be separated by fractional distillation. They are more readily obtained pure from toluene.

**Orthocresol** (1—2) is a crystalline solid, fusible at 31°–31.5° (87.8°–88.7° F.), which assumes a blue color with ferric chlorid.

**Metacresol** (1—3) is obtainable by the action of $P_2O_5$ on thymol. It is a colorless liquid, whose odor resembles that of phenol. It boils at 201° (393.8° F.), and does not solidify at —75° (—103° F.).

**Paracresol** (1—4) is a crystalline solid, fusible at 36° (96.8° F.), boiling at 198° (388.4° F.), having a phenol-like odor; colored blue by ferric chlorid. **Creolin**—an antiseptic less poisonous than phenol, consists chiefly of cresols. **Lysol** is impure paracresol, mixed with fat and saponified.

**Creasote — Creasotum** (U. S.)— is a complex mixture containing phenol, cresol, **creasol**, $C_8H_{10}O_2$, **guaiacol**, $C_7H_8O_2$ (see pyrocatechol), and other substances, obtained from wood-tar, and formerly extensively used as an antiseptic. It is an oily liquid, colorless when freshly prepared, but becoming brownish on exposure to light. It has a burning taste and a strong, peculiar odor. It boils at 203° (397.4° F.), and does not solidify at —27° (—16.6° F.).

**Xenols—Xylenols.**—Theoretically there are six possible xenols which are **dimethyl phenols**, $C_6H_3(CH_3)_2OH$; two derivable from orthoxylene, three from metaxylene and one from paraxylene. They

have all been produced synthetically. There are also three possible xenols which are ethyl phenols, $C_6H_4(C_2H_5)OH$.

**Thymol—3-Methyl-6-isopropyl phenol**—*Cymylic phenol*—$C_6H_3(OH)_{(1)}(CH_3)_{(3)}(C_3H_7)_{(6)}$,—exists, accompanying cymene and thymene, $C_{10}H_{16}$, in essence of thyme, from which it is obtained. It is also prepared synthetically from cuminic aldehyde, $C_6H_4(CHO)_{(1)}(C_3H_7)_{(4)}$.

It crystallizes in large, transparent, rhombohedral tables; has a peppery taste, and an agreeable, aromatic odor. It fuses at 44° (111.2° F.), and boils at 230° (446° F.); is sparingly soluble in water, very soluble in alcohol and ether. With the alkalies it forms definite compounds, which are very soluble in water. Its reactions are very similar to those of phenol.

Thymol is an excellent deodorizing and antiseptic agent, possessing the advantage over phenol of having itself a pleasant odor.

**Aristol** is diiodo-thymol, a dibenzenic compound, produced by the action of a solution of I in KI upon an aqueous solution of thymol in the presence of KHO. It is an inodorous, yellowish-red powder, insoluble in $H_2O$, very sparingly soluble in alcohol, readily soluble in ether and in chloroform. It is decomposed by heat and by light and is said to be a non-poisonous antiseptic.

**Carvacrol—2-Methyl-5-isopropyl phenol**—$C_6H_3(OH)_{(1)}(CH_3)_{(2)}(C_3H_7)_{(5)}$—an isomere of thymol, exists in many essential oils, and is obtained by the action of iodin upon camphor; by the action of potash in fusion upon cymene sulfonic acid, $C_{10}H_{13}SO_3H$; or by a transposition of the atoms of another isomere, **carvol**, which exists in caraway oil. It is an oil, boiling at 233°–235° (451.4°–455° F.). Heated with $P_2O_5$, it yields orthocresol.

### SUBSTITUTED PHENOLS.

Phenol is a monosubstituted derivative, and hence still contains five H atoms which may be replaced by other elements or radicals, to produce di- or tri- or poly-substituted derivatives of benzene, which will be ortho, meta or para, etc., according to the relations of the introduced groups to the OH, already existing in phenol, or to the $C_nH_{2n+1}$ and OH groups in its superior homologues.

**Chlorophenols.**—The three monochlorinated compounds are obtainable from the corresponding chloranilins. **Orthochlorophenol** (1—2) is a colorless liquid, boils at 175°–176° (347°–348.8° F.), converted into pyrocatechol by KHO. **Metachlorophenol** (1—3) is a liquid, boiling at 214° (417.2° F.). KHO converts it into resorcinol. **Parachlorophenol** (1—4) is a crystalline solid, fusible at 37° (98.6° F.), converted into quinol by fusion with KHO. Di-, tri-, and penta-chlorophenols are also known.

**Bromophenols** correspond in method of formation and properties with the Cl derivatives. **2-4-6 Tribromophenol**—$C_6H_2.OH.Br_3$—is the precipitate formed on adding bromin water to phenol solution. It forms white crystals, fusing at 92° (197.6° F.), insoluble in water, soluble in alcohol and ether. It is used as an antiseptic in diphtheria under the name **Bromol.** Paramonochlorophenol and orthomonobromophenol have been used for the same purpose.

**Iodophenols** are formed by the action of iodin and $K_2S$ upon phenol in the presence of excess of alkali, or from the corresponding amidophenols. Like the chlorin and bromin derivatives, they yield the corresponding diphenol by the action of KHO in fusion. A triiodophenol, formed by the action of solution of I in $K_2S$ upon an alkaline solution of phenol, has been proposed as a substitute for iodoform under the name **annidalin.** (See also pp. 404, 409, 418.)

## DIATOMIC, OR DIHYDRIC PHENOLS.

Diatomic phenols are derived from the benzenic hydrocarbons by the substitution of two (OH) groups for two atoms of hydrogen. In obedience to the laws of substitution already discussed, three such compounds exist, corresponding to each hydrocarbon.

**Pyrocatechol**—*Pyrocatechin—Oxyphenic acid—Orthodioxy-benzene* —$C_6H_4(OH)_{2\,(1,2)}$ is obtained from catechin or from morintannic acid by dry distillation; also by the action of KHO on orthochlor- or orthoiodo-phenol, or by decomposing its methyl ether, **guaiacol,** by HI at 200° (392° F.). It crystallizes in short, square prisms; fuses at 104° (219.2° F.), and boils at 245.5° (473.9° F.). Readily soluble in water, alcohol, and ether. Its aqueous solution gives a dark green color with $Fe_2Cl_6$ solution, changing to violet on addition of $NH_4HO$, $NaHCO_3$, or tartaric acid. Its acid sulfuric ester exists in the urine.

**Monomethyl-pyrocatechuic Ether—Guaiacol**—$C_6H_4.OH.(OCH_3)_{(2)}$—exists in beech-wood tar, from which an impure (60–90%) guaiacol is obtained as a yellowish liquid, sp. gr. 1.133, boiling at 206°–207°, by distillation. Pure guaiacol is obtained from this by crystallization at low temperature; by heating pyrocatechol with potassium-methyl sulfate and KHO; also from vanillin (p. 399), and from veratrol. It is a crystalline solid, fuses at 33° (91.4° F.), boils at 205° (401° F.), soluble in 50 parts of water. Guaiacol is used in the treatment of phthisis both on account of its germicidal action, and upon the theory that it forms compounds with the toxalbumins (q. v.), which are readily eliminated. It is also used in numerous forms of combination: in its carbonic esters, as **styracol**=cinnamyl-guaiacol, as **benzosol**=benzoyl-guaiacol, as **thiocol**=guaiacol-potassium sulfonate, and in combination with salicylic acid.

**Dimethyl-pyrocatechuic Ether—Veratrol**—$C_6H_4(OCH_3)_{2(1,2)}$—is an oil, crystallizing at 15° (59° F.), formed by distilling veratric acid (p. 405), or by acting upon the potassium salt of guaiacol with methyl iodid.

**Resorcinol**—*Resorcin*—*Metadioxy-benzene*—$C_6H_4(OH)_{2(1,3)}$ is obtained by the action of fused KHO on metachlor- or iodophenol. It is also prepared by dry distillation of extract of Brazil wood.

It forms short, thick, colorless and odorless, rhombic prisms. Fuses at 104° (219.2° F.), and boils at 271° (519.8° F.). It is very soluble in water, alcohol, and ether. Its aqueous solution is neutral in reaction, and intensely sweet. With $Fe_2Cl_6$ its solutions assume a dark-violet color, which is discharged by $NH_4HO$. Its ammoniacal solution, by exposure to air, assumes a pink color, changing to brown and, on evaporation, green and dark blue. Heated with phthalic anhydrid at 195° (383° F.) it yields fluoresceïn (p. 396). It dissolves in fuming $H_2SO_4$, forming an orange-red solution, which becomes darker, changes to greenish-black, then to pure blue, and finally to purple on being warmed.

Resorcinol, heated with sodium nitrite and $H_2O$ to about 150° (302° F.) yields a blue pigment known as lacmoid, which behaves like litmus with acids and alkalies, but is more sensitive.

**Quinol**—*Hydroquinone*—*Paradioxy-benzene*—$C_6H_4(OH)_{2(1,4)}$ is formed by fusing paraiodo-phenol with KHO at 180° (356° F.), by dry distillation of oxysalicylic acid or of quinic acid, and by the action of reducing agents on quinone. It forms colorless, rhombic prisms, which fuse at 169° (336.2° F.). Readily soluble in water, alcohol, or ether. Its aqueous solution is turned red-brown by $NH_4HO$. Oxidizing agents convert it into quinone.

**Orsinol**—*Orsin*—*Dimetadioxy toluene*—$C_6H_3(CH_3)_{(1)}(OH)_{(3)}(OH)_{(5)}$—a homologue of resorcinol, exists in nature in those lichens which are used as sources of archil and litmus (*Rocella tinctoria*, etc.). It crystallizes in six-sided prisms; is sweet; readily soluble in water, alcohol, or ether; fuses at 58° (136.4° F.). Its aqueous solution is colored violet-blue by $Fe_2Cl_6$. It unites with $NH_3$ to form a compound which absorbs O from the air, and is converted into orceïn, $C_7H_7NO_3$; a dark-red or purple body, which is the chief constituent of the dye-stuff known as archil, cudbear, French purple, and litmus.

### TRIATOMIC, OR TRIHYDRIC PHENOLS.

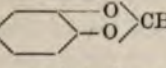
**Phloroglucin**—$C_6H_3(OH)_{3(1,3,5)}$—is obtained by the action of potash upon phloretin, quercitrin, maclurin (see Glucosids), catechin, kino, etc. It crystallizes in rhombic prisms, containing 2Aq; is very sweet; and very soluble in water, alcohol, and ether.

**Pyrogallol**—*Pyrogallic acid*—$C_6H_3(OH)_{3(1,2,3)}$—is formed when gallic acid (p. 406) is heated to 200° (392° F.). It crystallizes in white needles; neutral in reaction; very soluble in water; very bitter; fuses at 132° (238° F.); boils at 210° (410° F.); poisonous. Its most valuable property is that of absorbing oxygen, for which purpose it is used in the laboratory in the form of a solution of potassium pyrogallate.

When pyrogallol is heated with half its weight of phthalic anhydrid for several hours at 190°–200° (374°–392° F.) it yields **pyrogallol phthaleïn, or galleïn,** a brown-red powder (or green crystals) which dissolves with a brown color in neutral solutions, the color changing to red with a faint excess of alkali.

**Oxyhydroquinone**—$C_6H_3(OH)_{3(1,2,4)}$—is produced by fusing quinone with KHO. It is crystalline, fuses at 140° (284° F.), very soluble in water and in ether.

## UNSATURATED PHENOLS.

These are derived from the benzenic hydrocarbons with unsaturated lateral chains (p. 387). Olefin monoxybenzenes, dioxybenzenes, trioxybenzenes, and a tetroxybenzene are known. They are aromatic oils of high boiling points, many derived from various plants. Included in this class are: **Chavicol, p-Allyl phenol**—$C_6H_4OH.(CH_2.CH:CH_2)_{(4)}$—occurs in an oil from certain peppers. Its isomere, **p-Propenyl phenol**, $C_6H_4.OH.(CH:CH.CH_3)_{(4)}$, is **p-anol**, whose methylic ether, $C_6H_4.O(CH_3).(CH:CH.CH_3)_{(4)}$, **p-propenyl anisol,** or **anethol**, exists in the oils of anise, estragon and fennel. Among the diphenols is **eugenol**, $C_6H_3.(CH_2.CH:CH_2)_{(1)}(OCH_3)_{(3)}(OH)_{(4)}$, **allyl 3-4-guaiacol**, an essential oil from pimenta, eugenia, and certain peppers. The corresponding dimethyl compound exists in bay-oil. **Safrol, Allyl 3-4 pyrocatechol methylene ether,** $CH_2:CH.CH_2$  , is present in oil of sassafras, and oil of Illicium. **Apiol**, from oil of parsley, is a complex methylene ether, corresponding to allyl tetraoxybenzene, $C_6H.(OH)_4.CH_2.CH:CH_2$.

## PHENOL DYES.

**Aurin**—$C_{19}H_{14}O_3$, and **Rosolic acid**—$C_{20}H_{16}O_3$—are substances existing in the dye obtained by the action of oxalic acid upon phenol in presence of $H_2SO_4$, known as **corallin, or pœonin,** which communicates to silk or wool a fine yellow-red color.

Aurin crystallizes in fine, red needles from its solution in HCl.

It is insoluble in $H_2O$, but soluble in HCl, alcohol, and glacial acetic acid. It forms a colorless compound with potassium bisulfite.

**Phthaleïns.**—These substances are produced by heating the phenols with phthalic anhydrid, $C_6H_4(CO)_2O$, water being at the same time eliminated.

Their constitution is that of a benzene nucleus, two of whose H atoms have been replaced by two acetone groups (CO), whose remaining valences attach them to two phenol groups by exchange with an atom of hydrogen (see p. 449).

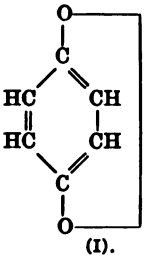
Thus phenol-phthaleïn, the simplest of the group, has the constitution, $C_6H_4\langle^{CO—C_6H_4(OH)}_{CO—C_6H_4(OH)}$. Phenol-phthaleïn is a yellow, crystalline powder, insoluble in water, but soluble in alcohol. Its alcoholic solution, perfectly colorless if neutral, assumes a brilliant magenta-red in the presence of an alkali. This property renders phenol-phthaleïn very valuable as an *indicator* of reaction.

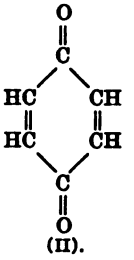
Resorcinol-phthaleïn — Fluoresceïn — $C_{20}H_{12}O_5$ — bears the same relation to resorcinol that phenol-phthaleïn does to phenol, and is obtained from resorcinol by a corresponding method. It is a dark-brown crystalline powder, which dissolves in ammonia to form a red solution, exhibiting a most brilliant green fluorescence. A tetrabromo-derivative of fluoresceïn is used as a dye under the name eosin.

## QUINONES.

The quinones are benzene derivatives in which two atoms of hydrogen are replaced by two oxygen atoms. The attachment of the –O.O– group is either ortho- or para-, never meta-. Ortho-quinones of the polybenzenic series, such as $\beta$ naphthoquinone and anthraquinone (p. 444), are well-known compounds, but the monobenzenic ortho-quinones are only known in their derivatives.

The monobenzenic para-quinones may be considered either as peroxids, the bonds of the benzene ring remaining intact (Formula I), or they may be considered as ring-ketones (Formula II), in which the two CO groups form a part of an oxidized hydroaromatic ring (p. 431). The former view is favored by the facts that the quinones are strong oxidizing agents, as are the peroxids in general, and that they yield monosubstituted derivatives by replacement of their oxygen by univalents, as benzoquinone forms p–dioxyben-


(I).


(II).

zene, $(HO)C\begin{smallmatrix}CH:CH\\CH.CH\end{smallmatrix}C(OH)$ on reduction, and p-dichlorobenzene, $ClC\begin{smallmatrix}CH:CH\\CH.CH\end{smallmatrix}CCl$, by the action of $PCl_5$. On the other hand, the existence of the CO= group in the quinones is indicated by the fact that they readily form oxims with hydroxylamin, a reaction characteristic of compounds containing CO= (p. 256), as benzoquinone forms quinone dioxim, $HO.NC\begin{smallmatrix}CH:CH\\CH.CH\end{smallmatrix}CN.OH$; and if, by reason of its oxidation of phenylhydrazin, benzoquinone forms no phenylhydrazone (p. 429) such compounds are formed by the naphthoquinones.

The quinones form a number of derivatives, by the introduction of alkyl, halogen, amido-, nitro, etc., groups for their hydrogen or oxygen. Among these are the **anils**, formed by substitution of $=N.C_6H_5$ for O, from which, in turn, an important series of blue and green dyes, the **indoanilin** or **indulin dyes** are derived.

**Quinone — Benzoquinone** — $C_6H_4:\begin{smallmatrix}O\\|\\O\end{smallmatrix}$ — is formed by the action of oxidants upon a variety of p-benzene derivatives, but best by limited oxidation of quinic acid. It crystallizes in golden-yellow prisms, f. p. 116° (240.8° F.), sublimes at ordinary temperatures, sparingly soluble in cold water, readily soluble in hot water, alcohol and ether. It has a peculiar, pungent odor, stimulates the lachrymal secretion, and irritates the skin. Reducing agents convert it into quinol.

## AROMATIC ALCOHOLS.

The alcohols (p. 239) corresponding to this series of hydrocarbons are isomeric with the phenols. They contain the characterizing group of the primary alcohols, $CH_2OH$; once if the alcohol be monoatomic, twice if diatomic, etc., and they yield on oxidation, first an aldehyde and then an acid. Thus: $C_6H_5.CH_2OH$ = benzylic alcohol; $C_6H_5.CHO$ = benzoic aldehyde; $C_6H_5.COOH$ = benzoic acid.

They are capable of yielding isomeric products of further substitution, ortho, para, or meta.

**Benzylic Alcohol—Benzoic Alcohol—Benzyl Hydrate**—$C_6H_5.CH_2OH$—does not exist in nature, and is of interest chiefly as corresponding to two important compounds, benzoic acid and benzoic aldehyde (oil of bitter almonds). It is obtained by the action of potassium hydroxid upon oil of bitter almonds, or by slowly adding sodium amalgam to a boiling solution of benzoic acid.

It is a colorless liquid; boils at 206.5° (403.7° F.); has an aromatic odor; is insoluble in water, soluble in all proportions in alcohol, ether, and carbon disulfid. By oxidation it yields, first, benzoic

aldehyde, $C_6H_5.CHO$; and afterward, benzoic acid, $C_6H_5.COOH$. By the same means it may be made to yield products similar to those obtained from the alcohols of the saturated hydrocarbons.

Secondary and tertiary aromatic alcohols are also known, such as phenyl-methyl carbinol, $C_6H_5.CHOH.CH_3$, and phenyl-dimethyl carbinol, $C_6H_5.COH(CH_3)_2$ (p. 240). The secondary alcohols yield ketones on oxidation (p. 400).

Di- and tri-hydric alcohols, such as the xylylene glycols, $C_6H_4(CH_2OH)_2$ (p. 251), and mesitylene glycerol, $C_6H_3.(CH_2OH)_{3(1,3,5)}$, are also known, as well as alcohols with unsaturated lateral chains, such as cinnamic alcohol, $C_6H_5.CH:CH.CH_2OH$, which occurs as its cinnamic ester in *storax*. It oxidizes to cinnamic aldehyde (p. 399) and cinnamic acid (p. 402).

### ALPHENOLS, OR OXYPHENYL ALCOHOLS.

These substances are intermediate in function between the alcohols and the phenols, and contain both substituted groups OH and $CH_2OH$.

**Saligenin**—*o-Oxybenzylic Alcohol*—$C_6H_4\langle^{CH_2OH}_{OH}$—is obtained from salicin (p. 413) in large, tabular crystals; quite soluble in alcohol, water, and ether. Oxidizing agents convert it into salicylic aldehyde, which by further oxidation yields salicylic acid. It is also formed by the action of nascent hydrogen on salicylic aldehyde.

### ALDEHYDES.

The aromatic aldehydes (p. 255) are the first products of oxidation of the aromatic alcohols. **Monaldehydes** containing one CHO group and **dialdehydes** containing two such groups are known.

The monaldehydes are formed: (1) By oxidation of the alcohols; (2) by decomposition of the alcohol bichlorids by water: $C_6H_5.CHCl_2 + H_2O = C_6H_5.CHO + 2HCl$. (3) By oxidation of the alcohol monochlorids by lead nitrate: $C_6H_5.CH_2Cl + O = C_6H_5.CHO + HCl$. (4) By the action of chromyl chlorid, $CrO_2Cl_2$, upon the hydrocarbons, and decomposition of the addition compound by water.

**Benzoic Aldehyde — Benzoyl hydrid** — $C_6H_5.CHO$ — is the main constituent of oil of bitter almonds, although it does not exist in in the almond (see p. 410). It is formed, along with hydrocyanic acid and glucose, by the action of water upon amygdalin. It is also formed by the general methods given above; by the dehydration of benzylic alcohol; by the dry distillation of a mixture in molecular proportions of calcium benzoate and formate; by the action of nas-

cent hydrogen upon benzoyl cyanid, etc. It is obtained from bitter almonds. The crude oil contains, besides benzoic aldehyde, hydrocyanic and benzoic acids and benzoyl cyanid.

It is a colorless oil, having an acrid taste and the odor of bitter almonds; sp. gr. 1.050; boils at 179.4° (354.9° F.); soluble in 30 parts of water, and in all proportions in alcohol and ether. Oxidizing agents convert it into benzoic acid, a change which occurs by mere exposure to air. Nascent hydrogen converts it into benzylic alcohol. With Cl and Br it forms benzoyl chlorid or bromid. $H_2SO_4$ dissolves it when heated, forming a purple-red color, which turns black if more strongly heated. It forms a series of products of substitution, haloid, nitro, amido, etc.

When perfectly pure, benzoic aldehyde exerts no deleterious action when taken internally; owing, however, to the difficulty of completely removing the hydrocyanic acid, the substances usually sold as *oil of bitter almonds*, *ratafia*, and *almond flavor*, are almost always poisonous, if taken in sufficient quantity. They may contain as much as 10–15 per cent. of hydrocyanic acid, although said to be "purified." The presence of the poisonous substances may be detected by the tests given on page 338.

**Salicylic Aldehyde**—*Salicyl hydrid*—*Salicylal*—*Salicylous acid*—o-*Oxybenzaldehyde*—$C_6H_4(OH)(CHO)_{(2)}$—exists in the flowers of *Spiræa ulmaria*, and is the principal ingredient of the essential oil of that plant. It is best obtained by oxidizing salicin (p. 413).

It is a colorless oil; turns red on exposure to air; has an agreeable, aromatic odor, and a sharp, burning taste; sp. gr. 1.173 at 13.5° (56.3° F.); boils at 196.5° (385.7° F.); soluble in water, more so in alcohol and in ether.

It is, as we should suspect from its origin, a substance of mixed function, possessing the characteristic properties of aldehyde and phenol. It produces a great number of derivatives, some of which are salts or esters, such as **p-methoxybenzaldehyde**, or **anisic aldehyde**, $C_6H_4(CHO)(OCH_3)_{(4)}$, a product of oxidation of **anethol** (p. 395).

**Vanillin—Methylprotocatechuic Aldehyde**—**m-Methoxy-p-oxybenzaldehyde**—$C_6H_3.CHO.(O.CH_3)_{(3)}(OH)_{(4)}$—a methylated dioxybenzaldehyde, is the odoriferous principle of vanilla. It is produced artificially by oxidation of **coniferin**, $C_{16}H_{22}O_8$, a glucosid occurring in coniferous plants (p. 411). It crystallizes in needles, fuses at 80° (176° F.), is sparingly soluble in water, readily soluble in alcohol or ether. It has a pungent taste and a persistent odor of vanilla. On exposure to air it becomes partly oxidized to **vanillic acid**, $C_8H_8O_4$.

**Cinnamic Aldehyde**—**β Phenyl-acrolein**—$C_6H_5.CH:CH.CHO$—is an example of the aromatic aldehydes with unsaturated lateral

chains. It is the chief constituent of oil of cinnamon; and is a colorless, aromatic oil, boiling at 247° (470.6° F.). It oxidizes readily to cinnamic acid (p. 402).

### KETONES.

The aromatic ketones (p. 261) are produced by the oxidation of the secondary aromatic alcohols (p. 398); $2C_6H_5.CHOH.CH_3 + O_2 = 2H_2O + 2C_6H_5.CO.CH_3$; or by the action of caustic potash upon the aromatic $\beta$ ketone-carboxylic acids (p. 408): $C_6H_5.CO.CH_2.COOH + 2KHO = C_6H_5.CO.CH_3 + H_2O + K_2CO_3$. Monoketones, diketones and triketones, containing one, two and three lateral chains with CO groups, are known. The monoketones, also called phenones, consist of a closed chain hydrocarbon group united to an open chain one by the group $(CO)''$. They may also be considered as benzene, into which fatty acid radicals have been substituted for hydrogen (see p. 448).

Phenyl-methyl Ketone—Acetyl benzene—Acetophenone—Hypnone—$C_6H_5.CO.CH_3$—is obtained by distilling a mixture of calcium benzoate and acetate; by the action of zinc-methyl upon benzoyl chlorid; or by the action of acetyl chlorid or bromid upon benzene in the presence of aluminium chlorid. It forms large crystalline plates, fusible at 20° (68° F.). It has been used as a hypnotic.

Acetophenone Oxim—$C_6H_5.C:(N.OH).CH_3$—is isomeric with acetanilid, $C_6H_5.NH(CO.CH_3)$, and is converted into that substance by the action of concentrated $H_2SO_4$ (p. 421).

### AROMATIC CARBOXYLIC ACIDS.

All six of the hydrogen atoms of benzene are replaceable by carboxyl groups, with formation of monocarboxylic acids, dicarboxylic acids, etc. There are also three series, o-, m-, and p-, of the bi-, tri-, and tetracarboxylic acids, and of the monocarboxylic acids above the first. These acids may be obtained by oxidation of the corresponding alcohols, or aldehydes, where these are known. Like the aliphatic acids, they may be considered as being derived from the hydrocarbons by substitution of hydroxyl for hydrogen in a lateral chain (p. 238).

### MONOCARBOXYLIC AROMATIC ACIDS—BENZOIC SERIES.

These acids are formed by many methods, among which the most important are: (1) By oxidation of the lateral chain in hydrocarbons

homologous with benzene. Thus toluene yields benzoic acid: $2C_6H_5.CH_3+3O_2=2C_6H_5.COOH+2H_2O$; (2) by oxidation of the corresponding alcohols and aldehydes; (3) by the action of sodium and carbon dioxid upon the monobromobenzenes: $C_6H_5Br+CO_2+2Na=NaBr+C_6H_5.COONa$; (4) by decomposition of the aromatic acid nitrils by acids or alkalies (pp. 278,373): $C_6H_5.CN+KHO+H_2O=C_6H_5.COOK+NH_3$. (5) By fusion of the aromatic sulfonic acids with sodium formate: $C_6H_5.SO_3Na+H.COONa=C_6H_5.COONa+NaHSO_3$.

The acids of this series form many derivatives. In some of these the carboxyl is modified, leaving either the radical **benzoyl**, $C_6H_5.CO$, as in **benzamid**, $C_6H_5.CO.NH_2$, or the trivalent group **benzenyl**, $C_6H_5.C$, as in **benzenyl-amidin**, $C_6H_5.C\langle^{NH_2}_{NH}$. In others the substitution occurs in the benzene ring, as in the oxy-, halogen-, and nitro-benzoic acids, etc., e. g. **anthranilic**, or **o-amido-benzoic acid**, $C_6H_4.COOH_{(1)}(NH_2)_{(2)}$.

**Benzoic Acid**—$C_6H_5.COOH$—exists in benzoin, tolu balsam, castoreum, and in several resins. It is obtained by the general methods given above; also from benzoin, and from the urine of herbivorous animals. The urine contains hippuric acid (p. 425), which, on decomposition, yields benzoic acid. Conversely, when benzoic acid is taken into the body in moderate doses it is eliminated as hippuric acid.

Benzoic acid crystallizes in white, transparent plates, odorless, sparingly soluble in cold water, readily soluble in hot water, in alcohol and in ether; fuses at 120° (248° F.), boils at 250° (482° F.), and sublimes at temperatures below its boiling point. Benzoic acid is not attacked by $HNO_3$. Heated with lime, it yields benzene and calcium carbonate: $C_6H_5.COOH+CaH_2O_2=C_6H_6+CaCO_3+H_2O$. The benzoates are all soluble, the least soluble being the ferric salt.

**Homologues of Benzoic Acid.**—These are of two kinds: (1) Those in which the carboxyl and hydrocarbon groups replace different hydrogen atoms, the **alkyl-benzoic acids**, as **cumic acid**, or **p-isopropyl benzoic acid**, $C_6H_5.(C_3H_7)_{(3)}(COOH)_{(4)}$. (2) Those in which the carboxyl is separated from the benzene ring by a hydrocarbon group, the **phenyl fatty acids**, as **phenyl-acetic acid**, $C_6H_5.CH_2.COOH$. In the terms above the first of this series there are place isomeres according to the distance from the ring in which the carboxyl is introduced. Thus **α phenyl-propionic acid**, $C_6H_5.CH\langle^{COOH}_{CH_3}$, and **β phenyl-propionic acid**, $C_6H_5.CH_2.CH_2.COOH$.

## POLYCARBOXYLIC AROMATIC ACIDS.

The di-, tri-, tetra-, penta-, and hexa-carboxylic aromatic acids are derived from benzene by substitution of from two to six car-

boxyls for hydrogen atoms. Of the superior homologues there exist a number of isomeres, increasing with the number of carbon atoms, according as the carboxyls are attached to the benzene ring, as in the phthalic acids, or are contained in lateral chains, as in phenyl-malonic acid, $C_6H_5.CH(COOH)_2$, and varying further by differences in orientation either in the benzene or the lateral chains.

**Phthalic Acids**—$C_6H_4(COOH)_2$—Ortho-, meta-, and para-phthalic acids are produced by oxidation of the corresponding bisubstituted benzene derivatives, and serve by their formation to determine whether a given compound is o-, m-, or p-.

**Phthalic Acid—Benzene-o-dicarboxylic acid**—$C_6H_4(COOH)_{2(1,2)}$—is obtained: (1) industrially by oxidation of naphthalene or tetrachloronaphthalene, for use in the manufacture of the phthaleïn dyes; (2) by oxidation of o-xylene, o-toluic acid, etc.; (3) by direct union of carbon monoxid with salicylic acid: $C_6H_4.OH.COOH+CO=C_6H_4(COOH)_2$; or with resorcinol: $C_6H_4(OH)_2+2CO=C_6H_4(COOH)_2$.

Phthalic acid crystallizes in prisms, sparingly soluble in cold water, readily soluble in hot water, alcohol, and ether, fuses at 213° (415.4° F.). Heated with $CaH_2O_2$, it is decomposed into benzene and $CO_2$. Nascent hydrogen converts it into hyrophthalic acids (p. 437). It is the only phthalic acid which yields an anhydrid.

**Isophthalic Acid—Benzene-m-dicarboxylic acid**—$C_6H_4(COOH)_{2(1,3)}$—is formed by oxidation of m-xylene, m-toluic acid, and other m-benzene bisubstituted derivatives. It crystallizes in fine needles, sparingly soluble in water, soluble in alcohol, fuses and sublimes above 300° (572° F.).

**Terephthalic Acid—Benzene-p-dicarboxylic acid**—$C_6H_4(COOH)_{2(1,4)}$—is formed by oxidation of p-xylene, p-toluic acid, and other p-benzene bisubstituted derivatives. It is insoluble in water, alcohol, and ether, and sublimes without melting.

### UNSATURATED AROMATIC CARBOXYLIC ACIDS.

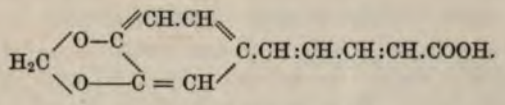
**Phenyl-olefin carboxylic Acids**—In some of these acids the carboxyl is attached to the benzene ring, as in **o-vinyl-benzoic acid**, $COOH.C_6H_4.(CH:CH_2)_{(2)}$. In those best known the carboxyl is in the lateral chain. They are obtained by oxidation of the corresponding alcohols or aldehydes (pp. 398, 399).

**Phenyl-acrylic Acids**—Two are known: **Atropic acid, α Phenyl-acrylic acid**, $C_6H_5.C\begin{matrix}\diagup COOH \\ \diagdown CH_2\end{matrix}$, a product of decomposition of **tropic acid** (p. 408); and **cinnamic acid, β phenyl-acrylic acid**, $C_6H_5.CH:CH.COOH$, which exists in several balsams and resins, and is produced in the decomposition of certain alkaloids. It is also formed from benzoic aldehyde by the action of acetyl chlorid: $CH_3.CO.Cl+$

$C_6H_5.CHO = C_6H_5.CH:CH.COOH + HCl$; or, with the intermediate formation of phenyl-p-oxypropionic acid, by the action of sodium acetate in presence of acetic anhydrid: $C_6H_5.CHO + CH_3.COONa = C_6H_5.CHOH.CH_2.COONa$, and $C_6H_5.CHOH.CH_2.COONa = C_6H_5.CH:CH.COONa + H_2O$. It crystallizes in prisms, fuses at 133° (271.4° F.), sparingly soluble in cold water, readily soluble in hot water. Oxidizing agents convert it into benzoic aldehyde and benzoic acid. It combines with hydrogen to form **hydrocinnamic, or β phenyl-propionic acid,** $C_6H_5.CH_2.CH_2.COOH$. Nitric acid converts it into a mixture of **o-** and **p-nitro-cinnamic acids,** the former of which is the starting point in a synthesis of indigo.

On heating with $H_2O$ or HCl, atropic acid is converted into two polymeric **isatropic acids, or diatropic acids,** $(C_9H_8O_2)_2$.

**Piperic Acid,** obtained by decomposition of piperin by heating with alcoholic KHO, is **3-4-Methylene-dioxy-cinnamenyl-acrylic acid:**




**Phenyl-propiolic acid**=$C_6H_5.C \vdots C.COOH$—is a **phenyl-acetylene carboxylic acid,** produced by the action of carbon dioxid upon phenyl-acetylene: $C_6H_5.C \vdots CH + CO_2 = C_6H_5.C \vdots C.COOH$. Its o-nitro derivative forms isatin (p. 466) when boiled with alkalies.

## PHENOL CARBOXYLIC ACIDS AND THEIR ESTERS.

These compounds have both hydroxyl and carboxyl attached to the benzene ring. They have the functions of phenol and of acid. They are formed: (1) by fusing the sulfobenzoic acids with alkalies: $C_6H_4(COOH)SO_3H + KHO = SO_3HK + C_6H_4(COOH)(OH)$, (p. 389). Also similarly from the haloid acids: $C_6H_4.Br.COOH + KHO = C_6H_4.OH.COOH + KBr$; (2) by fusion of the homologues of phenol with caustic potash, the methyl of the hydrocarbon lateral chain is oxidized to carboxyl; (3) by oxidation of the phenol-aldehydes by fusion with caustic alkalies; (4) by saponification of their esters, produced by oxidizing the sulfuric or phosphoric esters of the homologues of phenol; (5) by heating the phenols with carbon tetrachlorid and caustic potash: $C_6H_5.OH + CCl_4 + 4KHO = C_6H_4.OH.COOH + 2H_2O + 4KCl$; (6) by the action of carbon dioxid upon the sodium phenates: $2C_6H_5.O.Na + CO_2 = C_6H_4.O.Na.COONa + C_6H_5.OH$.

Di-, tri-, and tetra-carboxylic oxyacids are known. But the best known of the oxyacids are monocarboxylic, and monoxy-, dioxy-, and trioxy-, corresponding to the phenols of like hydroxyl content.

### MONOXY-MONOCARBOXYLIC ACIDS.

**Oxybenzoic Acids**—$C_6H_4.OH.COOH$.—Of the three isomeric acids the meta-, f. p. 200° (392° F.), and the para-, f. p. 210° (410° F.), acids are obtained by the action of KHO on the corresponding bromobenzoic acids.

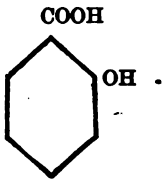
**Salicylic Acid—o-Oxybenzoic Acid**—f. p. 155° (311° F.), occurs free, accompanied by salicylic aldehyde (p. 399), in *Spiræa ulmaria* and, as its methylic ester, in oil of wintergreen. It is also formed by decomposition of salicin, coumarin or indigo. It is produced synthetically by the above reactions and, industrially, by heating sodium phenate in a current of carbon dioxid. The reaction is not $C_6H_5.ONa + CO_2 = C_6H_4.OH.COONa$, but $2C_6H_5.ONa + CO_2 = C_6H_5.OH + C_6H_4.ONa.COONa$.

Salicylic acid crystallizes in prisms or needles, sparingly soluble in cold water, readily soluble in hot water, alcohol and ether, sweet and acid in taste. When heated, it distils in part unchanged, while a part loses oxygen and yields salol and xanthone, $C_{13}H_{10}O_2$; or salol, carbon dioxid and water (see below). With Cl and Br it forms products of substitution. With fuming $HNO_3$ it forms a nitro-acid and, finally, picric acid. With ferric chlorid it gives a fine violet color. Nascent hydrogen causes rupture of the ring, with formation of pimelic acid (p. 289) as a final product. Salicylic acid and its salts and esters are used as antiseptics and as antirheumatics.

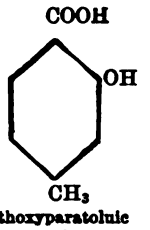
**Phenyl Salicylate—Salol**—$C_6H_4.OH.COO(C_6H_5)$—is formed by heating salicylic acid to 220° (428° F.): $2C_6H_4.OH.COOH = C_6H_4.OH.COO(C_6H_5) + CO_2 + H_2O$; also by the action of $POCl_3$ on a mixture of salicylic acid and phenol. It is a white, crystalline powder, faintly aromatic in taste and odor, almost insoluble in water, soluble in alcohol, ether and benzene, fuses at 43° (110° F.). It is not decomposed by weak acids, but is saponified by alkalies to form salicylic acid and phenol; hence it passes unchanged through the stomach to be decomposed in the intestine: $C_6H_4.OH.COO(C_6H_5) + H_2O = C_6H_4.OH.COOH + C_6H_5.OH$.

**Acetol Salicylate—Salacetol**—$C_6H_4.OH.COO(CH_2.CO.CH_3)$—the ester of the keto-alcohol, acetol (p. 263), is formed by the action of monochloracetone on sodium salicylate. It crystallizes in plates, sparingly soluble in water, readily soluble in alcohol, fusible at 71° (159.8° F.). It is saponified by alkalies with formation of acetol and salicylic acid, and is hence substituted for salol as a medicine when the formation of phenol is undesirable. Like acetol and its other esters, it reduces Fehling's solution.

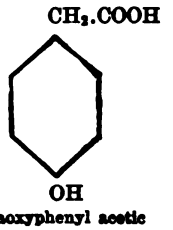
The superior homologues of the salicylic acids are either alkyl substituted derivatives of the oxybenzoic acids or oxyphenyl fatty acids:




o-Salicylic acid.




Orthoxyparatoluic acid.



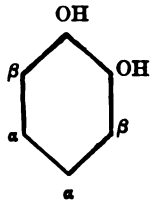

Paraoxyphenyl acetic acid.

**Paraoxyphenylacetic acid** and **paraoxyphenylpropionic acid**, $C_6H_4(OH)_{(1)}(CH_2.CH_2.COOH)_{(4)}$, the latter also called **hydroparacoumaric acid**, exist in the urine in "alkaptonuria," accompanied by **paraoxyphenylglycollic acid**, $C_6H_4(OH)_{(1)}(CHOH.COOH)_{(4)}$, and the dioxycarboxylic acids mentioned below. They are products of decomposition of protein material.

### DI- AND TRIOXYMONOCARBOXYLIC ACIDS.

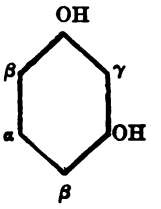
**Dioxycarboxylic Acids.**—The six isomeres corresponding to the three diphenols are known, as well as numerous alkyl derivatives, such as vanillic, isovanillic and veratric acids, which are derived from protocatechuic acid. The relations of these acids are shown by the following formulæ:

PYROCATECHOL.



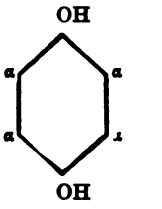

α = 3.4-Dioxybenzoic.
= Protocatechuic.
β = 2.3-Dioxybenzoic.

RESORCINOL.

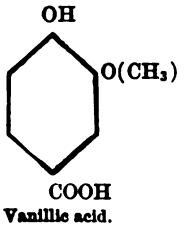



α - Resorcylic,
= 3.5-Dioxybenzoic,
β - Resorcylic,
= 2.4-Dioxybenzoic.
γ Resorcylic,
= 2.6-Dioxybenzoic.

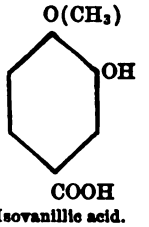
QUINOL.



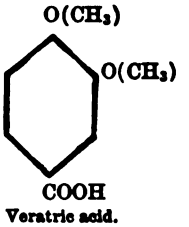

2.5-Dioxybenzoic,
= Gentisinic,
= Hydroquinone-carboxylic.




Vanillic acid.



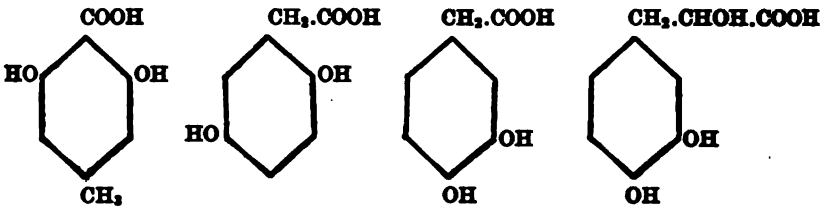

Isovanillic acid.




Veratric acid.

**Protocatechuic Acid—3.4-Dioxybenzoic Acid**—$C_6H_3(COOH)_{(1)}(OH)_{2(3,4)}$—exists in the fruit of the star-anise, and is produced from many resins by fusion with KHO. It is formed by fusion of the corresponding dibromobenzoic acid, and other similar derivatives, with KHO.

The superior homologues of dioxycarboxylic acids are either dioxytoluic acids, etc., such as orsellinic acid, or dioxy-phenyl fatty acids, such as homogentisinic acid:




2.6-Dioxyparatoluic. = Orsellinic. 2.5-Dioxyphenyl-acetic. = Homogentisinic. 2.4-Dioxyphenyl-acetic. = Homoprotocatechuic. 2.4-Dioxyphenyl-lactic. = Uroleucic (?)

**Homogentisinic acid, or glycosuric acid,** exists in the urine in "alkaptonuria," probably accompanied by **homoprotocatechuic and uroleucic acids,** as well as by the monoxy-monocarboxylic acids mentioned above.

**Trioxycarboxylic Acids.**—Three of the six possible acids are known, two derived from pyrogallol, one from phloroglucin (p. 394).

**Gallic Acid**—$C_6H_3(COOH)_{(1)}(OH)_{3(3,4,5)}$—exists in nature in certain leaves, seeds and fruits. It is best obtained from nut-galls, which contain its glucosid, gallo-tannic acid. It is formed when bromo-protocatechuic acid is fused with caustic potash. It crystallizes in long, silky needles with 1Aq, odorless, acidulous in taste, sparingly soluble in cold water, very soluble in hot water and in alcohol. Its solutions are acid. When heated to 210–215° (410–419° F.) it yields $CO_2$ and pyrogallol (p. 395). Its solutions reduce the salts of silver and of gold; they do not precipitate gelatin nor the salts of the alkaloids, as does tannin; and they give a blue-black precipitate with $Fe_2Cl_6$.

**Tannins—Tannic Acids**—are substances of vegetable origin, principally derived from leaves, barks and seeds. They are amorphous, soluble in water, astringent, capable of precipitating albumin, of forming imputrescible compounds with the gelatinoids (leather), and give green or blue colors with the ferric salts.

Pure tannic acid has been obtained by removal of water from gallic acid: $2C_7H_6O_5=C_{14}H_{10}O_9+H_2O$; it is, therefore, **digallic acid.** It exists in gall-nuts, excrescences produced upon oak trees by the punctures of certain insects (gallo-tannic acid). It is colorless, amorphous, odorless, very soluble in water, less so in alcohol, almost

insoluble in ether. It forms a dark-blue liquid (ink) with solutions of ferric salts or, after exposure to air, with ferrous salts.

**Caffetannic Acid**, $C_{30}H_{18}O_{16}$, exists in saline combination in coffee and Paraguay tea. It colors the ferric salts green, precipitates the salts of quinin and cinchonin, but not tartar emetic or gelatin, as tannic acid does. It yields **caffeic acid, or 3-4-dioxycinnamic acid,** $C_9H_8O_4$, on decomposition. **Cachoutannic acid**, obtained from catechu, is soluble in water, alcohol and ether. It precipitates gelatin, but not tartar emetic, and colors ferric salts grayish-green. **Morintannic acid, or maclurin,** $C_{13}H_{10}O_6$, is a yellow, crystalline substance, obtained from fustic. It is more soluble in alcohol than in water. Its solutions precipitate greenish-black with ferric salts, yellow with lead acetate, brown with tartar emetic and yellowish-brown with cupric sulfate. **Quercitannic acid,** $C_{19}H_{16}O_{10}$, is the tannin of oak bark. It is a red powder, sparingly soluble in water, which forms a violet-red precipitate with ferric salts. **Quinotannic acid** exists in cinchona barks, in combination with the alkaloids. It is light yellow, soluble in water, alcohol and ether, astringent, but not bitter in taste. It is colored green by ferric salts. Dilute $H_2SO_4$ decomposes it with formation of **quina red**, an amorphous substance, which yields protocatechuic and acetic acids on further decomposition.

## ALCOHOL-, ALDEHYDE-, AND KETONE-CARBOXYLIC AROMATIC ACIDS; AND THEIR ESTERS.

The aromatic **alcohol-acids** are of two classes: (1) **alcohol-carboxylic acids**, in which the group $CH_2OH$ is attached to the benzene ring, and (2) **phenyl-paraffin alcohol-acids**, which contain either $CH_2OH$; CHOH or $(CHO)'''$ in a lateral chain.

The three **oxymethyl-benzoic acids** are the best known of these acids, and of these the **o-acid,** $C_6H_4(COOH)_{(1)}(CH_2OH)_{(2)}$, a white powder, fusible, with decomposition, at 118° (244.4° F.), produced by the action of boiling alkalies upon

**Phthalid** — $C_6H_4\langle^{CO_{(1)}}_{CH_{(2)}}\rangle O$ — its lactone (p. 320), which is formed by several reactions, as by the reduction of phthalic anhydrid by nascent hydrogen. Phthalid crystallizes in needles, fusible at 73° (163.4° F.), sparingly soluble in cold water, rather soluble in hot water. Reducing agents convert it into orthotoluic acid; oxidizing agents into phthalic acid. It forms a number of substituted phthalids, among which is meconin (see also p. 449).

**Meconin — 5-6-Dimethyloxyphthalid** — $(CH_3O)_{2(5,6)}C_6H_2\langle^{CO_{(1)}}_{CH_{(2)}}\rangle O$ — the lactone of **meconinic acid**, and the earliest known lactone,

exists in opium, and is also formed by the action of reducing agents upon narcotin. It is also formed by reduction of the corresponding aldehyde-acid, opianic acid, $(CH_3O)_2C_6H_2\langle^{COOH}_{CHO}$, a product of decomposition of narcotin and of hydrastin. Meconin, or opianyl, is a neutral, non-poisonous, crystalline substance, which gives a fine green color, changing to red after 24 hours, with $H_2SO_4$.

The phenyl-paraffin alcohol-acids may be considered as derived from the aliphatic oxyacids (p. 289) by substitution of phenyl, $C_6H_5$, or phenylene, $C_6H_4$, for hydrogen in the alcohol or hydrocarbon groups. They are mono- or di-carboxylic and mono- or dioxy-, and, in the higher terms, $\alpha$, $\beta$, etc.

Phenylglycollic Acid—Mandelic Acid—$C_6H_5.C^*HOH.COOH$—is the lowest term of the series, and exists in three optical isomeres. The inactive acid is formed by the action of nascent hydrogen upon benzoic aldehyde, $C_6H_5.CHO$, or upon benzoyl-formic acid, $C_6H_5CO.COOH$. Oxidising agents convert it first into benzoyl-formic acid and then into benzoic acid.

Phenyllactic Acids—$\alpha$ and $\beta$ phenyllactic acids, $C_6H_5.COH\langle^{CH_3}_{COOH}$, and $C_6H_5.CH_2.CHOH.COOH$, and $\alpha$ and $\beta$ phenylhydracylic acids, $C_6H_5.C^*H\langle^{COOH}_{CH_2OH}$, and $C_6H_5.C^*H\langle^{CH_2.COOH}_{OH}$, are known (p. 292). Alpha-phenylhydracrylic acid is tropic acid, the inactive modification of which is a product of decomposition of atropin and hyoscyamin. It is also formed synthetically from atropic acid (p. 402).

The dioxy-alcohol acids are derived from the acids of the glyceric series (p. 293), as $\alpha$ phenylglyceric acid, $CH_2OH.C(C_6H_5)OH.COOH$.

The dicarboxylic alcohol-acids are either benzyl- or phenyl-alcohol acids such as benzyl-tartronic acid, $(C_6H_5.CH_2).COH:(COOH)_2$; or phenylene oxydicarboxylic acids, such as carbomandelic acid, $C_6H_4\langle^{COOH}_{CHOH.COOH}$. The phenylene acids readily form phthalid acids (lactones) more stable than themselves, such as phthalid-acetic acid, $C_6H_4\langle^{CO—O}_{CH.COOH}$.

The aromatic aldehyde acids contain the carboxyl and aldehyde groups attached to the benzene ring, as in opianic acid (above).

In the ketone acids the ketone group $(CO)''$ is necessarily in a lateral chain. In some of these acids the ketone and carboxyl groups are in different lateral chains, as in aceto-benzoic acid, $C_6H_4\langle^{COOH}_{CO.CH_3}$, but in most of them the two groups are in the same chain, and are $\alpha$, $\beta$, $\gamma$, etc., according to the removal of the CO from the COOH group. Thus benzoyl-formic acid, $C_6H_5.CO.COOH$, is $\alpha$, and benzoyl acetic acid, $C_6H_5.CO.CH_2.COOH$, is $\beta$.

Besides the above there are also known: **Phenyl-alcohol-ketone acids,** such as **benzoyl-glycollic acid,** $C_6H_5.CO.CHOH.COOH$; **phenyl-diketone-acids,** such as **benzoyl-pyroracemic acid,** $C_6H_5.CO.CH_2.CO.COOH$; **phenyl-ketone-dicarboxylic acids,** such as **benzoyl-malonic acid,** $C_6H_5.CO.CH:(COOH)_2$; and **phenylene-ketone-dicarboxylic acids,** such as **phthalonic acid,** $C_6H_4\begin{smallmatrix}CO.COOH\\COOH\end{smallmatrix}$.

## PHENYLIC ETHERS — GLUCOSIDS.

The oxids of the aromatic series, corresponding to the aliphatic ethers (p. 299), and containing two cyclic hydrocarbon groups united by an oxygen atom, properly belong among the dibenzenic compounds (p. 384), but are more conveniently considered here.

**Phenyl Ether — Diphenyl Oxid** — $(C_6H_5)_2O$ — is formed by heating phenol with aluminium chlorid, or with zinc chlorid: $2C_6H_5.OH = C_6H_5.O.C_6H_5 + H_2O$, and by other more circuitous methods. It crystallizes in long needles, having the odor of geranium, soluble in alcohol and in ether. Corresponding to it are a number of derivatives, formed by substitution of various univalents for the remaining phenol hydrogen.

The **mixed oxids,** containing a phenyl and an alkyl group, such as anisol, $C_6H_5.O.CH_3$, are the phenyl ethers (p. 391), derived from phenol and its homologues.

## GLUCOSIDS.

The name "glucosid" was first applied to certain natural products, some of which are the active constituents of medicinal plants, which, on decomposition by dilute mineral acids, yield glucose and some other substance. Subsequently, it was found that the sugars derived from some of these substances differ from glucose; some are pentoses, others hexoses; some monosaccharids, others disaccharids; some aldoses, others ketoses. On the other hand, the second product of decomposition has been of the most varied character, phenols, alphenols, alcohols, oxyphenols, monobenzenic or dibenzenic, but, in all those natural glucosids which have been investigated, always a cyclic compound, containing a phenolic or an alcoholic group. The glucosids have usually been regarded as esters of glucose, etc., since the alcoholic character of the sugars has been recognized, but, as the union of the sugar and benzenic factors is through an oxygen atom, and not by replacement of the hydrogen of a carboxyl, they are more properly regarded as ethers (p. 299), formed by union of an aldose or ketose remainder with one of a phenolic or alcoholic

benzenic compound, with elimination of $H_2O$. The constitution of the glucosids cannot, however, be considered as established, as no natural glucosid has been obtained synthetically, although the products of decomposition of some are comparatively simple compounds. It is to be supposed that the union takes place through the aldehyde group, as the glucosids do not reduce Fehling's solution and do not form osazones. They probably contain some such grouping as: $CH_2OH.(CHOH)_3.CH\overset{O}{\diagup\!\!\diagdown}CH.O.B$, in which B represents the benzenic factor.

The glucosids are decomposed (hydrolized) by heating with dilute acids, or, at very slightly elevated temperatures, by certain enzymes, such as emulsin, which exists in almonds, myrosin, in mustard seeds, the invertin of malt, and salivary and intestinal enzymes. They are very slowly hydrolyzed by heating with water under pressure, if at all; and only a few of them are decomposed by alkalies.

The glucosids yielding pentoses on hydrolysis are more properly designated pentosids.

**Phenyl Glucosid—Glucosyl phenate**—$C_6H_{11}O_5.O.C_6H_5$—is the simplest of the glucosids, and is an artificial product, formed by mixing alcoholic solutions of acetochlorhydrose (p. 320) and potassium phenate, $CHO.(CH.CO_2.CH_3)_4.CH_2Cl + C_6H_5.O.K + 4H_2O = CHO.(CHOH)_4.CH_2.O.C_6H_5 + KCl + 4CH_3.COOH$. It forms soluble, crystalline needles, fusible at 172°, and is decomposed by emulsin into glucose and phenol.

Among the more important of the natural glucosids are the following:

**Æsculin**—$C_{15}H_{16}O_9$—which exists in the rinds of horse-chestnuts. It forms colorless crystals, sparingly soluble in water, the solutions having a brilliant blue fluorescence, even when very dilute. It forms a yellow solution with $HNO_3$, which becomes deep blood-red on supersaturation with ammonia. It is decomposed by dilute mineral acids, or by emulsin, into glucose and **æsculetin**, $C_9H_6O_4$, which is probably a dioxy-derivative of coumarin (p. 463): $C_6H_2(OH)_2\langle\begin{matrix}CH:CH\\ |\\ O—CO\end{matrix}$.

**Amygdalin**—$C_{20}H_{27}NO_{11}$—exists in the bitter almond, in the kernels of peach- and plum-pits, apple- and pear-seeds, and a great variety of other plants. It crystallizes in colorless prisms with 3Aq, easily soluble in water, insoluble in ether, odorless, and bitter. It is decomposed by dilute mineral acids, or by emulsin, into two molecules of glucose and one each of benzoic aldehyde and hydrocyanic acid: $C_{20}H_{27}NO_{11} + 2H_2O = 2C_6H_7O(OH)_5 + C_6H_5.CHO + CNH$. By the action of alkalies, particularly by heating with $BaH_2O_2$, amygdalin yields **amygdalic acid**, $C_{20}H_{28}O_{13}$, of which amygdalin appears to be

the nitril: $C_6H_7O(OH)_4.O.C_6H_7O(OH)_3.O.CH(C_6H_5)CN$, and this, on splitting off of the sugar, first forms the nitril of mandelic acid (p. 408): $C_6H_5.CHOH.CN$, the subsequent decomposition of which into $C_6H_5.CHO$ and HCN is evident. Amygdalin itself is non-poisonous, but its ready decomposition, with formation of the extremely poisonous hydrocyanic acid, is a prolific source of cyanic poisoning.

**Antiarin**—$C_{14}H_{20}O_5$—is the poisonous constituent of the juice of *Upas antiar*, used as an arrow-poison. **Apiin**, $C_{27}H_{32}O_{16}$, is a glucosid obtained from parsley and other umbelliferous plants. **Arbutin**, $C_{12}H_{16}O_7$, accompanied by **methyl-arbutin**, occurs in *Arbutus uva-ursi*, and yields hydroquinone on decomposition. It gives a blue color with ferric chlorid. **Carminic acid**, $C_{17}H_{18}O_{10}$, is the coloring principle of cochineal and of carmine, and is a weak dibasic acid. It is a dark-purple substance, decomposed by acids into an inactive, unfermentable sugar, and **carmine-red**, $C_{11}H_{12}O_7$.

**Coniferin**—$C_{16}H_{22}O_8$—is a glucosid occurring in the inner bark (cambium) of coniferous plants, and in asparagus and the sugar-beet. It crystallizes in silky, white needles, sparingly soluble in water, faintly bitter. With phenol and concentrated hydrochloric acid it assumes an intense blue color (pine-shaving reaction, p. 390). It is decomposed by emulsin into glucose and coniferyl alcohol, which is a hydroxyl-oxymethyl cinnamyl alcohol (p. 398): $CH_3\text{-}\overset{HO}{\underset{O}{\diagdown\diagup}}C_6H_3.CH:CH.CH_2OH$. By oxidation with chromic acid it forms **glucovanillin**, $C_6H_{11}O_5.O.C_6H_3(OCH_3)CHO$, which is decomposed by emulsin into glucose and vanillin: methylprotocatechuic aldehyde (p. 399). Glucovanillin, containing an aldehyde group, forms a crystalline compound with phenylhydrazin, and an oxim. By further oxidation it forms **glucovanillic acid**, and by reduction, the corresponding alcohol.

**Convolvulin**—is a glucosid of undetermined composition, which is the active constituent of jalap. It is a yellowish, slightly acid, amorphous material, sparingly soluble in water, easily soluble in alcohol, forming a deep-red solution with $H_2SO_4$. **Crocin**, $C_{44}H_{70}O_{28}$, is the coloring matter of saffron, an amorphous, yellow substance, soluble in water and in alcohol. With concentrated $H_2SO_4$, it gives a deep-blue color, changing to violet, red, and brown. It is decomposed by dilute hydrochloric acid into a dextrogyrous hexose, having half the reducing power of glucose, and **crocetin**, $C_{24}H_{46}O_9$, an orange-yellow substance soluble in alcohol and ether, but almost insoluble in water. **Cyclamin**, $C_{20}H_{34}O_{11}$, is a white, crystalline glucosid existing in various species of *Cyclamen*. **Daphnin**, $C_{15}H_{16}O_9$, occurs in the bark of *Daphne mezereum*, and other species of *Daphne*. It crystallizes in colorless prisms, bitter and astringent, sparingly soluble in water and in ether, soluble in alcohol. It is colored bluish by ferric chlorid.

It is decomposed into glucose and daphnetin, $C_9H_6O_4$, isomeric with æsculetin (above). Daphnetin has been shown to be a dioxycoumarin, having the hydroxyls in the positions 1, 2, by its synthesis by condensation of pyrogallol (p. 394) and malic acid: $C_6H_3(OH)_{3(1,\,2,\,3)}+COOH.CH_2.CHOH.COOH=H.COOH+2H_2O+C_6H_2(OH)_{2(1,\,2)}\begin{matrix}O_{(2)}-CO\\ |\\ CH_{(4)}:CH\end{matrix}$.

**Digitalis Glucosids.**—The active substance of digitalis consists, in part at least, of a glucosid, or glucosids, probably accompanied by products of decomposition, but the chemistry of these compounds requires further investigation. **Digitonin**, $C_{27}H_{44}O_{13}$(?), is the most abundant constituent of the "amorphous digitalins," and has little or no therapeutic value. It is an amorphous, white solid, very soluble in water, which crystallizes from its alcoholic solutions. It is decomposed by dilute hydrochloric acid into **digitonein**, or **digitogenin**, $C_{15}H_{24}O_4$, glucose and galactose. **Digitalin**, $(C_5H_8O_2)_n$(?), separates in amorphous or nodular masses from its alcoholic solution. On decomposition it yields **digitaliresin**, $C_{16}H_{22}O_2$, glucose and **digitalose**, $C_7H_{14}O_5$. It has the physiological action of digitalis upon the heart, and is the principal constituent of "Homolle's digitalin." **Digitoxin**, $C_{21}H_{32}O_7$(?), crystallizes in fine needles, insoluble in water, soluble in hot alcohol and in chloroform. It is the most actively poisonous of the digitalis glucosids, and is the chief constituent of "Nativelle's digitalin." Digitalin gives a color-reaction which is not given by digitoxin: it forms a golden-yellow or brownish solution with concentrated $H_2SO_4$, which becomes violet-red by the action of bromin-vapor.

**Frangulin**—$C_{21}H_{20}O_9$—is a pentosid, existing in the bark of *Rhamnus frangula*. It forms yellow crystals, almost insoluble in water, which, on decomposition, yield emodin (p. 445), and the pentose, **rhamnose**, $CH_3.(CHOH)_4.CHO$. **Fraxin**, $C_{16}H_{18}O_{10}$, accompanies æsculin in the horse-chestnut and occurs in ash-bark. It is a white, crystalline solid, sparingly soluble in water, its solutions showing a blue fluorescence. It is decomposed into glucose, and **fraxetin**, a methyl ether of trioxycoumarin, $C_6H(OH)_2(O.CH_3)\begin{matrix}O-CO\\ |\\ CH:CH\end{matrix}$ (page 463). **Helleborein**, $C_{26}H_{44}O_{15}$, and **helleborin**, $C_{36}H_{42}O_6$, are two poisonous, crystalline glucosids occurring in black hellebore. On decomposition they both yield glucose, and the former **helleboretin**, $C_{14}H_{20}O_3$(?), and the latter **helleboresin**, $C_{30}H_{38}O_4$ (?).

**Hesperidin**—$C_{22}H_{26}O_{12}$ (?)— occurs in unripe oranges, lemons, etc. It forms crystalline needles, very sparingly soluble in most solvents, except hot acetic ether, soluble in dilute alkaline solutions. It is one of the few glucosids yielding both a hexose and a pentose on decomposition; being split by heating with dilute $H_2SO_4$ into glu-

cose, rhamnose, and **hesperetin**, $C_{16}H_{14}O_6$. Hesperetin is further decomposed by heating with caustic potash into phloroglucin (p. 394) and **hesperetic, or isoferulic acid**, $C_6H_3(CH:CH.COOH)_{(1)}(OH)_{(3)}(O.CH_3)_{(4)}$, a derivative of cinnamic acid (p. 402). It therefore contains two benzene nuclei.

**Indican**—$C_{26}H_{31}NO_{17}$—is a glucosid occurring in the indigo plant. It is a yellow or light-brown syrup, which cannot be dried without decomposition, bitter and disagreeable in taste, acid in reaction, and soluble in water, alcohol and ether. It is very prone to decomposition. Even slight heating decomposes it into leucin, **indicanin**, $C_{20}H_{23}NO_{12}$, and **indiglucin**, $C_6H_{10}O_6$. A characteristic decomposition is that by which it yields indigo-blue (p. 466) and indiglucin, along with other products: $2C_{26}H_{31}NO_{17}+4H_2O=C_{16}H_{10}N_2O_2+6C_6H_{10}O_6$.

**Jalapin** — *Scammonin* — $C_{34}H_{56}O_{16}$ — is the glucosid of scammony. It is an insipid, colorless, amorphous substance, decomposable into **jalapinol**, $C_{16}H_{30}O_3$, and glucose. **Myronic acid**, $C_{10}H_{19}NS_2O_{10}$, exists as its potassium salt in the seeds of black mustard. Potassium myronate crystallizes in prisms; very soluble in water, almost insoluble in alcohol, which are decomposed by boiling with $BaH_2O_2$, or by **myrosin**, an enzym which accompanies it in the mustard seeds, into glucose, allyl isothiocyanate (p. 377) and monpotassic sulfate. **Naringin**, $C_{21}H_{26}O_{11}$, is a pentosid, occurring in the blossoms and fruit of a Java orange. It forms yellow crystals, bitter in taste, sparingly soluble in water, decomposable by dilute acids into rhamnose and **naringenin**, $C_{15}H_{12}O_5$, which is in turn decomposed by alkalies into phloroglucin and **naringenic acid**, or **p-coumaric acid**, $C_9H_8O_3$. **Phloridzin**, $C_{21}H_{24}O_{10}$, occurs in the root-bark of apple and other fruit trees. It crystallizes in flat, colorless needles, bittersweet in taste, difficultly soluble in cold water, but readily soluble in hot water and in alcohol. It is decomposed by heating with dilute acids, or even by prolonged boiling with water, into a crystalline, dextrogyrous hexose, **phlorose**, and **phloretin**, $C_{15}H_{14}O_5$, which is further decomposed by hot alkalies into phloroglucin and **phloretic, or p-oxyhydratropic acid**, $C_6H_4(OH).C_2H_4.COOH$ (p. 403). **Quercitrin**, $C_{36}H_{38}O_{20}$, is the coloring principle of a yellow dye-stuff called **flavin**, obtained from *Quercus tinctoria*. It crystallizes in yellow needles, sparingly soluble in water. It is a pentosid, and is decomposable by acids into rhamnose and **quercetin**, $C_{24}H_{16}O_{11}$, a benzopyrone derivative (p. 464). **Quinovin, or quinovic acid**, $C_{38}H_{62}O_{11}$ (?), is a bitter substance, occurring in false cinchona barks, decomposable into a peculiar pentose, **quinovose**, $C_6H_{12}O_5$, and **quinovic acid**, $C_{32}H_{48}O_6$.

**Salicin** — $C_{13}H_{18}O_7$ — occurs in willow bark. It is a white, crystalline substance, insoluble in ether, soluble in water and in alcohol,

very bitter in taste. Concentrated $H_2SO_4$ colors it intensely red, the color being discharged by addition of water. It is decomposed by emulsin, by saliva, or by mineral acids into glucose and saligenin (p. 398). When taken into the economy it is converted into salicylic aldehyde and acid, which are eliminated in the urine. Populin, a glucosid from poplar bark, is benzoyl-salicin.

Solanin—$C_{42}H_{87}NO_{15}$(?)—is a glucosid having basic properties, an alkaloid-glucosid, occurring in a variety of plants of the genus *Solanum*. It crystallizes in white, silky needles, acrid and bitter in taste, insoluble in water, sparingly soluble in alcohol and in ether. By the action of hot dilute acids it is decomposed into glucose and a basic substance, solanidin. When not heated, solanin combines with acids to form uncrystallizable salts. Cold, concentrated $H_2SO_4$ colors it orange-yellow, and finally forms with it a brown solution. Nitric acid dissolves it, the solution being at first colorless, afterwards rose-pink.

### ANHYDRIDS AND ACID HALOIDS.

The aromatic acidyls form oxids, or anhydrids, and haloid compounds, corresponding to those of the aliphatic acidyls, and produced by similar methods (pp. 310, 311).

Benzoic Anhydrid—$(C_6H_5.CO)_2O$—is formed from benzoyl chlorid by several methods: as by a reaction between benzoyl chlorid and silver benzoate: $C_6H_5.CO.Cl+C_6H_5.COOAg=(C_6H_5.CO)_2O+AgCl$. It is a crystalline solid, f. p. 42°, b. p. 360°.

Phthalic Anhydrid—$C_6H_4(CO)_2:O$—being formed from a dicarboxylic acid, is produced from a single molecule of the acid, with elimination of $H_2O$. It is formed by fusing phthalic acid. It sublimes in needles; f. p. 128° (262.4° F.); sparingly soluble in cold water, soluble in hot water, with regeneration of the acid, very soluble in alcohol and in ether. It combines with phenols to form phthaleïns (p. 396).

Benzoyl Chlorid—$C_6H_5.CO.Cl$—was the first obtained of the acidyl haloids. It is formed by the action of hydrochloric acid upon benzoic acid, in presence of phosphorus pentoxid: $C_6H_5.COOH+HCl=C_6H_5.CO.Cl+H_2O$; or by the action of chlorin upon benzoic aldehyde: $C_6H_5.CHO+Cl_2=HCl+C_6H_5.CO.Cl$; or, along with acetyl chlorid, by the action of chlorin upon benzyl acetate: $CH_3.COO(CH_2.C_6H_5)+2Cl_2=C_6H_5.CO.Cl+CH_3.CO.Cl+2HCl$. The two chlorids are separated by fractional distillation.

Benzoyl chlorid is a colorless liquid; b. p. 198°; having a penetrating odor. With silver (or mercuric) cyanid it forms benzoyl cyanid: $C_6H_5.CO.Cl+AgCN=C_6H_5.CO.CN+AgCl$. It acts readily upon the polyatomic alcohols and upon the hexoses, when shaken

with their solutions in presence of caustic soda. With the hexoses pentabenzoyl compounds are formed, and crystallize out: $CHO.C_5H_6(OH)_5+5C_6H_5.CO.Cl=CHO.C_5H_6(O.CO.C_6H_5)_5+5HCl$. This is a reaction utilized for the isolation of hexoses and polyatomic alcohols. A similar reaction, similarly utilized, occurs with the diamins, in which insoluble, crystalline, dibenzoyl compounds are formed: $C_2H_4(NH_2)_2+2C_6H_5.CO.Cl=C_2H_4(NH.CO.C_6H_5)_2+2HCl$.

## AROMATIC SULFUR-DERIVATIVES—SULFONIC ACIDS.

Many **thio-aromatic compounds** are known, as **thiophenol**, $C_6H_5.SH$, **phenyl sulfid**, $(C_6H_5)_2S$, and **thio-benzoic acid**, $C_6H_5.COSH$. But the most important of the aromatic compounds containing sulfur are the

**Sulfonic Acids** (p. 322), monobasic acids containing the group $SO_3H$, formed by the union of the aromatic hydrocarbon, or derivative, with $H_2SO_4$ with elimination of OH from the acid and H from the aromatic compound, a process called "sulfonation": $C_6H_6+H_2SO_4=C_6H_5.SO_3H+H_2O$. The aromatic and polybenzenic sulfonic acids are formed much more readily than the corresponding aliphatic acids, and, being acid and soluble, are largely used as dyes. They are usually produced by the action of fuming $H_2SO_4$ upon the aromatic compound, with or without the aid of heat.

The sulfonic acids are not decomposed by boiling with alkaline solutions, but their salts, when fused with caustic alkalies, yield phenols: $C_6H_5.SO_3K+KHO=C_6H_5.OH+K_2SO_3$. Distilled with potassium cyanid they yield nitrils: $C_6H_5.SO_3K+KCN=C_6H_5.CN+K_2SO_3$. By the action of $PCl_5$ they are converted into their chlorids, e. g. $C_6H_5.SO_2Cl$, which may be, in turn, converted into **sulfinic acids**, **sulfones**, etc. They are easily soluble in water, and may be separated from their solutions, as sodium salts, by the addition of NaCl

**Benzene-monosulfonic Acid**—$C_6H_5.SO_3H$—is formed by dissolving benzene in weak fuming sulfuric acid at a slightly elevated temperature, and diluting with $H_2O$. It crystallizes in extremely soluble, deliquescent plates with $1\frac{1}{2}$ Aq.

Three **benzene-disulfonic acids**—$C_6H_4(SO_3H)_2$—ortho-, meta- and para-, are known, also one **benzene-trisulfonic acid**—$C_6H_3(SO_3H)_3$.

Three **toluene-sulfonic acids**—$C_6H_4(CH_3).SO_3H$—ortho-, meta- and para-, have been obtained. By the action of a mixture of ordinary and fuming sulfuric acids upon toluene at a temperature not exceeding 100° (212° F.), a mixture of the ortho- and para- acids is produced. When this is treated with $PCl_5$, it is converted into a mixture of **para-** and **ortho-toluene sulfonic chlorids**—$C_6H_4.CH_3.SO_2Cl$. The ortho-chlorid, when acted on by dry ammonia and ammonium

carbonate, is converted into **ortho-toluene sulfimid** — $C_6H_4.CH_3.SO_2NH_2$. This product, when oxidized by potassium permanganate, is converted into **benzoyl-sulfonic imid** — $C_6H_4.CO.SO_2NH_2$ — or **saccharin** — an odorless, crystalline powder, having great sweetening power, its sweet taste being still detectable in a dilution of 1–50,000. Sparingly soluble in water and in ether, readily in alcohol. Its solutions are acid in reaction. When heated with $Na_2CO_3$ it is carbonized and gives off an odor of benzene. It is not attacked by $H_2SO_4$.

Another series of sulfonic derivatives is obtained from the phenols. Among them is:

**Ortho-phenol sulfonic Acid** — **Sozolic acid** — **Aseptol** — $C_6H_4.(OH)_{(1)}(SO_3H)_{(2)}$ — which is prepared by the action of cold concentrated $H_2SO_4$ upon phenol. It is a reddish, syrupy liquid, soluble in $H_2O$ in all proportions, has a faint and not disagreeable odor. It prevents fermentation and putrefaction, and is a non-poisonous, non-irritant antiseptic. The salts of this and the corresponding para- and meta-acids have been used as antiseptics and insecticides, under the name of **sulfo-carbolates**, *e. g.* **Sodii sulfo-carbolas** (U. S.).

**Guaiacol-sulfonic Acid** is used in medicine as its potassium salt, $C_6H_3(OH)_{(1)}(OCH_3)_{(2)}SO_3K$, under the name **thiocol.**

**Salicyl-sulfonic acid** — $C_6H_4.COOH.O.SO_3H$ — is a crystalline solid, formed by the action of strong $H_2SO_4$ on salicylic acid. It is easily soluble in $H_2O$. It has been recommended as a test for albumin.

**Diiodo-phenol monosulfonic Acid** — $C_6H_2I_2.OH.SO_3H$ — is used as an antiseptic and astringent, in the form of its salts under the name **sozoiodol**; and **Diiodo-resorcinol monosulfonic acid** — $C_6HI_2.(OH)_{(1-3)}.SO_3H$ — is also used as an antiseptic having but slight poisonous qualities, under the name **picrol.**

## NITROGEN-CONTAINING DERIVATIVES OF BENZENE.

The nitrogen derivatives of benzene are very numerous, of great variety of structure, and include among their number several substances of great industrial value.

They may be classified into five principal groups: (1) The **nitro-compounds**, derived from other benzenic compounds by substitution of $NO_2$ for H, and the **nitroso-compounds**, containing the nitroso group, NO; (2) The $\beta$ **hydroxylamin compounds**, containing the group $-N\langle^{OH}_{H}$, and their nitroso derivatives; (3) the **amido-** and **imido-compounds**, containing $NH_2$ and NH, the **aromatic amins, amids**, and **amido-acids**, and their derivatives; (4) the **azo-** and

**diazo-compounds** and their numerous derivatives, containing the grouping —N=N—; (5) the **hydrazins**, containing the grouping =N—N=, and their nitroso derivatives.

### NITRO- AND NITROSO-COMPOUNDS

**Nitro-benzenes.**— These contain the nitro group directly attached to the carbon of the benzene ring. They are produced by the action of fuming $HNO_3$, or a mixture of $HNO_3$ and $H_2SO_4$, upon the hydrocarbons: $C_6H_6+HNO_3=C_6H_5.NO_2+H_2O$. They are yellow liquids, sparingly soluble in water. Their most important property is their ready reduction, first to $\beta$ hydroxylamin compounds: $C_6H_5.NO_2+2H_2 = C_6H_5.NH.OH + H_2O$; and then to amido-compounds: $C_6H_5.NH.OH + H_2 = C_6H_5.NH_2 + H_2O$ (p. 419).

**Mono-nitro-benzene—Nitro-benzol—Nitro-benzene—Essence of Mirbane** — $C_6H_5.NO_2$ — is obtained by the moderated action of fuming $HNO_3$, or of a mixture of $HNO_3$ and $H_2SO_4$ on benzene.

It is a yellow, sweet liquid, with an odor of bitter almonds; sp. gr. 1.209 at 15° (59° F.); boils at 213° (415.4° F.); almost insoluble in water; very soluble in alcohol and in ether. Concentrated $H_2SO_4$ dissolves, and, when boiling, decomposes it. Boiled with fuming $HNO_3$, it is converted into **dinitro-benzenes.** It is converted into anilin by reducing agents.

It has been used in perfumery as *artificial essence of bitter almonds;* but as inhalation of its vapor, even largely diluted with air, causes headache, drowsiness, difficulty of respiration, cardiac irregularity, loss of muscular power, convulsions, and coma, its use for that purpose is to be condemned. Taken internally, it is an active poison.

Nitro-benzene may be distinguished from oil of bitter almonds (benzoic aldehyde) by $H_2SO_4$, which does not color the former; and by the action of acetic acid and iron filings, which convert nitro-benzene into anilin, whose presence is detected by the reactions for that substance (p. 420).

**Dinitrobenzenes.**— The three dinitrobenzenes are produced by boiling the mono-nitro compound with fuming $HNO_3$. The meta-compound predominates, and may be separated by fractional crystallization from alcohol. It crystallizes in plates, fusible at 90° (194° F.), and is used in the preparation of certain dyes, and of explosives, such as **roburite, sicherheit,** etc. The gases resulting from such explosives are poisonous.

**Nitrotoluenes.** — $C_6H_4.CH_3.NO_2$—The o- and p- compounds are produced together by nitration of toluene, and exist in the commercial nitro-benzene. They may be separated by fractional distillation, the

o- compound boiling at 218° (424.4° F.), and the p- at 230° (446° F.). By reduction they yield the corresponding toluidins, largely used in the color industry.

**Nitro-phenols — Mononitro-phenols** — $C_6H_4(NO_2)OH$ — (1—2), (1—3) and (1—4) are formed by the action of $HNO_3$ on $C_6H_5.OH$. The ortho compound (1—2) crystallizes in large yellow needles, sparingly soluble, and capable of distillation with steam. The meta and para compounds are both colorless, non-volatile, crystalline bodies. Methyl chlorid converts nitrophenols into the corresponding nitro-anisols, $C_6H_4.OCH_3.NO_2$, and ethyl iodid into nitrophenetols, $C_6H_4$-$OC_2H_5.NO_2$, which by reduction yield anisidins and phenetidins (p. 423). Two dinitro-phenols, $C_6H_3.OH(NO_2)_{2(6-4)}$, and $C_6H_3.OH$-$(NO_2)_{2(6-6)}$ are obtained by the action of strong nitric acid on phenol or on ortho- or para-mononitro phenol. They are both solid, crystalline substances, converted by further nitration into picric acid.

**Trinitro-phenols**—$C_6H_2(NO_2)_3OH$.—Two are known; (1) **Picric acid—Carbazotic acid—Trinitro-phenic acid**—$(NO_2)$ in 2—4—6. It is formed by nitration of phenol, or of 1—2—4 or 1—2—6 dinitro-phenols, and also by the action of $HNO_3$ on indigo, silk, wool, resins, etc. It crystallizes in yellow plates or prisms, odorless, intensely bitter (πικρὸς = bitter); acid in reaction; sparingly soluble in water, very soluble in alcohol, ether, and benzene; it fuses at 122.5° (252.5 F.), and may, if heated with caution, be sublimed unchanged; but, if heated suddenly or in quantity, it explodes with violence. It behaves as a monobasic acid, forming salts, which are for the most part soluble, yellow, crystalline, and decomposed with explosion when heated.

Picric acid colors silk and wool yellow. It is used as a reagent for the alkaloids, with many of which it forms crystalline precipitates, as it also does with many other substances. It is sometimes added to beer and to other food articles, to communicate to them either a bitter taste or a yellow color. Its solutions give yellow, crystalline precipitates with K salts; green precipitates with ammoniacal $CuSO_4$; and an intense red color when warmed with alkaline KCN solution. It is poisonous,

**Nitro-cresols**—$C_6H_3.CH_3.OH.NO_2$.—The o- and p- compounds are known. They are readily converted into the corresponding dinitro compounds, $C_6H_2.CH_3.OH.(NO_2)_2$. The 2-6 dinitro compound is used as a dye in the form of its sodium salt, under the name *Victoria orange*, or *saffron surrogate*. It is poisonous.

The **nitroso-phenols** are obtained by the action of nitrous acid upon the phenols; or by the action of hydroxylammonium chlorid upon the quinones.

**p-Nitroso-phenol—Quinoxim**—$C_6H_4.(OH)_{(1)}(NO)_{(4)}$, or $C_6H_4\begin{cases}O\\|\\N.OH\end{cases}$—(pp. 334, 396), crystallizes in needles, and explodes when heated. **Dinitroso-resorcinol** — $C_6H_2(OH)_{2(1\cdot3)}(NO)_{2(4\cdot6)}$ is a brown, explosive substance, used as a green dye, *solid green*.

**Nitro-acids**, such as **o-**, **m-**, and **p-nitro-benzoic acids**, $C_6H_4$-$COOH.NO_2$, etc., are known. They yield amido-acids by reduction.

### β HYDROXYLAMIN COMPOUNDS.

Compounds derived from hydroxylamin by substitution of phenyl-alkyl radicals for extra-hydroxyl hydrogen are formed as intermediate products of reduction of the nitro-benzenes (pp. 417, 428).

**β-Phenylhydroxylamin**—$C_6H_5.N\begin{cases}OH\\H\end{cases}$—is an intermediate product of reduction between nitro-benzene and amido-benzene: : $C_6H_5.NO_2+2H_2=C_6H_5.N\begin{cases}OH\\H\end{cases}+H_2O$, and $C_6H_5.NO_2+3H_2=C_6H_5.NH_2+2H_2O$. It is readily oxidized to nitroso-benzene and other products, and it reduces Fehling's solution and ammoniacal $AgNO_3$ solution. Mineral acids cause its intramolecular rearrangement to p-amido-phenol: $C_6H_5.N\begin{cases}OH\\H\end{cases}=C_6H_4(OH)_{(1)}(NH_2)_{(4)}$. With nitrous acid it forms a nitroso derivative : $C_6H_5.N\begin{cases}OH\\NO\end{cases}$. It is a crystalline solid; f. p. 81°; and forms a crystalline, colorless hydrochlorid.

### AMIDO-COMPOUNDS.

The **amido-benzenes** are the counterparts of the aliphatic primary monamins (p. 326). They are obtained by reduction of the corresponding nitro-compounds. The reaction is, with moderate reduction, not so simple as is expressed by the equation: $C_6H_5.NO_2+3H_2=$ $C_6H_5.NH_2+2H_2O$, but several important intermediate products are formed (pp. 417, 428, and above).

**Anilin—Amido-benzene**—*Amido-benzol*—**Phenylamin**—*Kyanol*—*Cristallin*—$C_6H_5.NH_2$—exists in small quantity in coal-tar, and is one of the products of the destructive distillation of indigo. It is prepared by the reduction of nitro-benzene by hydrogen: $C_6H_5.(NO_2)+3H_2=C_6H_5(NH_2)+2H_2O$ (see above); the hydrogen being liberated in the nascent state in contact with nitro-benzene by the action of iron filings on acetic acid.

Pure anilin is a colorless liquid; has a peculiar, aromatic odor, and an acrid, burning taste; sp. gr. 1.02 at 16° (60.8° F); boils at 184.8° (364.6° F.); crystallizes at —8° (17.6° F.); soluble in 31

parts of cold water, soluble in all proportions in alcohol, ether, carbon disulfid, etc. When exposed to air it turns brown, the color of the commercial "aniline oil," and, finally, resinifies. It is neutral in reaction. Oxidizing agents convert it into rosanilin (p. 450), from which blue, violet, red, green, or black derivatives are obtained. Cl, Br, and I act upon it violently to produce products of substitution. Concentrated $H_2SO_4$ converts it, according to the conditions, into sulfanilic, or p-amido-benzene sulfonic acid, $C_6H_4(NH_2)_{(1)}$, $(SO_2H)_{(4)}$, or disulfanilic acid, or anilin 2-4 disulfonic acid, $C_6H_3$-$(NH_2)_{(1)}$,$(SO_2H)_{2(2,4)}$. With acids it unites, after the manner of the ammonia, to form salts, most of which are crystallizable, soluble in water, and colorless, although by exposure to air, especially if moist, they turn red. The sulfate has been used medicinally. Potassium permanganate oxidizes it to nitro-benzene. Heated with $H_2SO_4$ and glycerol it produces quinolin, and substituted quinolins may be obtained by a similar reaction from substituted anilins.

Anilin itself, when taken in the liquid form or by inhalation, is an active poison, producing symptoms similar to those caused by nitro-benzene (p. 417). Its salts, if pure, seem to have but slight deleterious action.

Anilin may be recognized by the following reactions: (1) With a nitrate and $H_2SO_4$: a red color; (2) cold $H_2SO_4$ does not color it alone; on addition of potassium dichromate, a fine blue color is produced, which, on dilution with water, passes to violet, and, if not diluted, to black. (3) With calcium hypochlorite: a violet color; (4) heated with cupric chlorate: a black color; (5) heated with mercuric chlorid: a deep crimson color; (6) in very dilute solution (1:250,000), anilin gives a rose color with chlorid of lime, followed by ammonium sulfhydrate.

Toluidins — $C_6H_4(CH_3)(NH_2)$. — Three toluidins, o-, m-, and p-, are known as the superior homologues of anilin. They occur in commercial anilin and play an important part in the production of anilin colors.

Xylidins — Amido-xylenes — $C_6H_3(CH_3)_2(NH_2)$. — Six compounds of this composition are known: two derived from ortho-xylene, three from meta-xylene, and one from para-xylene. Five of them exist in commercial xylidin.

The toluidins and xylidins yield products of substitution and addition similar to those of anilin.

Carbodiimids are substances having the general formula $C\langle^{NR}_{NR}$, in which RR are two univalent radicals, usually belonging to the aromatic series. They are prepared from the sulfureïds, by loss of the elements of carbon oxysulfid, COS, by the action of heat or of oxydants.

**Derivatives of Anilin.**—By the substitution of other radicals or elements for the remaining hydrogen atoms of the benzene nucleus, or for the hydrogen atoms of the amido group, $NH_2$, a great number of derivatives, including many isomeres, are produced.

**Chloranilins.**—Three **monochloranilins** are known, of which two, ortho- (1—2) and meta- (1—3), are liquid. The other, para- (1—4), is solid and crystalline.

Four **dichloranilins**, 1—2—4, 1—2—5, 1—3—5, and 1—3—4, are known, all solid and crystalline.

Two **trichloranilins**, 1—2—4—6 and 1—2—4—5, are known, both solid and crystalline.

The corresponding **bromanilins** are also known: also a **tetrabromanilin**, 1—2—3—4—6, and a **pentabromanilin**, $C_6(NH_2)Br_5$.

Of the possible **iodanilins**, but four have been described: **Metamoniodanilin** (1—3); **paramoniodanilin** (1—4); the **diiodanilin** (1—2—4); and the **triiodanilin** (1—2—4—6).

**Nitranilins.**—The three isomeres, **ortho-, meta-,** and **paramononitranilins**, $C_6H_4(NH_2)(NO_2)$, are formed by imperfect reduction of the dinitro-benzenes.

Two **dinitranilins**, $C_6H_3(NH_2)(NO_2)_2$ (1—2—4) and (1—2—6), are known.

A single **trinitranilin**, $C_6H_2(NH_2)(NO_2)_3$ (1—2—4—6), has been obtained by the action of alcoholic ammonia upon the ethylic or methylic ether of picric acid. It is also called **picramid.**

**Anilids.**—These are compounds in which one of the H atoms of the amido group has been replaced by an acid radical. Or they may also be considered as amids, whose remaining hydrogen has been more or less replaced by phenyl, $C_6H_5$.

**Acetanilid—Antifebrin—Phenyl-acetamid**—$C_6H_5(NH.CO.CH_3)$—is obtained either by heating together anilin and glacial acetic acid for several hours, or, better, by the action of acetyl chlorid on anilin. It forms colorless, shining, crystalline scales; fuses at 112.5° (234.5° F.), and volatilizes unchanged at 295° (563° F.). It is sparingly soluble in cold water, soluble in hot water and in alcohol.

When acetanilid is heated with an equal weight of $ZnCl_2$, **flavanilin**, a colored substance having a fine green fluorescence, and soluble in warm dilute HCl, is produced.

By herbivorous animals acetanilid is eliminated as **para-amido phenol**, $C_6H_4(OH)_{(1)}(NH_2)_{(4)}$; by carnivorous animals partly in that form, but mostly as **orthoxy-carbanil**, $C_6H_4(N.CO)_{(1)}(OH)_{(2)}$.

Acetanilid and its derivatives in the urine respond to the **indophenol reaction**: Boiled a few minutes with HCl, a colorless solution is formed, which, on addition of $H_2O$ and solution of phenol

in chlorinated lime solution, assumes a turbid, dirty red color, and on addition of ammonia an indigo-blue.

By the further substitution of a group ($CH_3$) in acetanilid, **methyl-acetanilid**, or **exalgine**, $C_6H_5.N(CH_3).C_2H_3O$, is produced. It is formed by the action of methyl-iodid upon sodium acetanilid, $C_6H_5.NNa.C_2H_3O$. It is a crystalline solid, sparingly soluble in $H_2O$, readily in dilute alcohol. Its odor is faintly aromatic.

Three **acettoluids**, $C_6H_3\langle^{CH_3}_{NH(C_2H_3O)}$, ortho-, meta-, and para-, are also known. The para- and meta- compounds seem to be almost inert, while the ortho- compound is highly poisonous.

The "anilin dyes" now so extensively used, even those made from anilin, are not compounds of anilin, but are salts of bases formed from it, themselves colorless, called rosanilins (see p. 450).

**Phenylamins — Phenylenediamins, etc.** — Anilin is the simplest representative of a large class of substances. It may be considered as benzene in which H has been replaced by $NH_2$, thus: $C_6H_5.NH_2$. Its superior homologues, derivable from the superior homologues of benzene, each have at least three isomeres, ortho-, meta-, and para-, according to the orientation of the groups $NH_2$ and $C_nH_{2n+1}$. Anilin may also be considered as ammonia in which H has been replaced by phenyl, $C_6H_5$, thus being a primary monamin (see p. 326), $^{C_6H_5}_{H_2}\}N$. The remaining two H atoms may be replaced by other radicals to form an almost infinite variety of secondary and tertiary phenylamins, precisely as in the case of the aliphatic monamins.

Possibly some of the ptomaïns are phenylamins. **Mydin**, $C_8H_{11}NO$, for example, is supposed to be **oxyphenyl ethylamin**, $C_6H_4\langle^{OH}_{CH_2.CH_2.NH_2}$. It is a powerful base, strongly alkaline, has an ammoniacal odor, is a strong reducing agent, is non-poisonous, and is produced after continued putrefaction at low temperatures.

Again, it is clear that, considering anilin as amido-benzene, the substitution of $NH_2$ is not limited to the introduction of one such group. There may be three **phenylenediamins**, $C_6H_4(NH_2)_2$, ortho-, meta-, and para-, three **triamido benzenes**, $C_6H_3(NH_2)_3$, etc.

**Meta-phenylenediamin** is converted into triamido azobenzene, **Bismark brown**, by nitrous acid, and is, therefore, used as a test for nitrites in water.

**Phenylcarbylamin — Phenyl Isocyanid — Isobenzonitril** — $C_6H_5.N:C$ — (p. 340) is formed when chloroform is heated with anilin and caustic potash in alcoholic solution (p. 235). It is a liquid, having a most persistent, disagreeable odor. Nascent hydrogen converts it into methyl anilin. Heated to 220° (428° F.), it is converted into its isomere, **benzonitril**, or **cyanobenzene**, $C_6H_5.CN$, which is a

liquid having an odor of bitter almonds; also formed by distilling potassium benzene sulfonate with potassium cyanid.

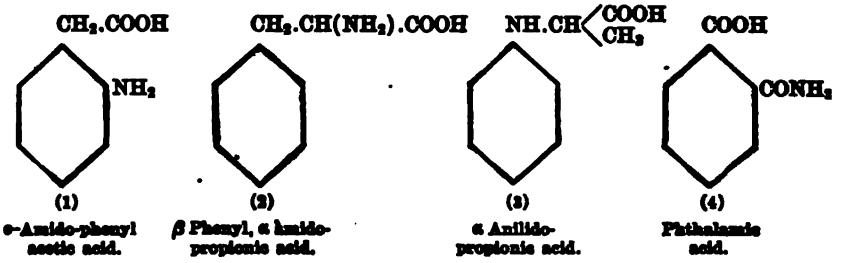
**Amido-phenols** — $C_6H_4\langle^{OH}_{NH_2}$—Three are known, ortho-, meta-, and para-, obtained by the action of reducing agents upon the corresponding nitro-compounds. Their methylic ethers, $C_6H_4\langle^{O(CH_3)}_{NH_2}$ are known as **anisidins**; and their ethylic ethers, $C_6H_4\langle^{O(C_2H_5)}_{NH_2}$ as **phenetidins.**

By the action of glacial acetic acid upon paraphenetidin, an aceto-derivative, **para-acetophenetidin,** $C_6H_4(OC_2H_5)_{(1)}.(NH.C_2H_3O)_{(4)}$, is formed. It is used as an antipyretic, under the name **phenacetine,** and is a colorless, odorless, tasteless powder, sparingly soluble in $H_2O$, readily soluble in alcohol, fuses at 135° (275° F.). Its hot aqueous solution is colored violet, changing to ruby-red, by chlorin water. The corresponding anisidin, **para-acetoanisidin,** $C_6H_4(OCH_3)_{(1)}(NH.C_2H_3O)_{(4)}$, **methacetine,** has also been used as a therapeutic agent. It crystallizes in white, shining, tasteless, odorless scales, fuses at 127° (260.6° F.), sparingly soluble in $H_2O$, readily soluble in alcohol. It responds to the indophenol reaction (p. 421).

**Aromatic acid amids** are formed by methods similar to those by which the aliphatic amids are produced, and resemble them in their reactions (p. 346). Thus **benzamid,** or **benzoyl amid,** $C_6H_5.CO.NH_2$, is formed by the action of benzoyl chlorid upon ammonia, $C_6H_5.CO.Cl+NH_3=HCl+C_6H_5.CO.NH_2$, as a crystalline solid, fusible at 130° (266° F.). Two formulæ of benzamid are possible: the amid formula, $C_6H_5.C\langle^{NH_2}_{O}$, and the imid formula, $C_6H_5.C\langle^{NH}_{OH}$. Derivatives corresponding to each are known.

The **aromatic amido-acids** greatly exceed the aliphatic (p. 361) in number and variety. They are: (1) **Amido-phenyl acids,** which may be considered either as aromatic acids, in which a ring hydrogen atom (or atoms) has been replaced by $NH_2$; or as aliphatic acids, in which amido-phenyl $(C_6H_4.NH_2)'$ has replaced H in a hydrocarbon group; (2) **phenyl-amido acids,** considered either as aromatic acids, in which $NH_2$ replaces H in a hydrocarbon group of a lateral chain, or as amido-aliphatic acids, in which phenyl $(C_6H_5)'$ has been substituted for H in a hydrocarbon group; (3) **anilido-acids**—aliphatic amido-acids in which phenyl has been substituted for H in $NH_2$. In this class are included the anilids of the dicarboxylic acids (p. 421), e. g., **oxanilic acid,** $OC\langle^{NH(C_6H_5)}_{COOH}$; (4) **amic acids** (p. 346), derived from the dicarboxylic aromatic acids by substitution of $NH_2$ for OH in one carboxyl group. Besides these there are

amido-acids referable to 1 and 3, in which the radical benzoyl, $C_6H_5.CO$, takes the place of phenyl, $C_6H_5$. The structure of these several acids is shown by the following formulæ:




**Amido-phenyl Acids**, of which anthranilic, or **o-amido-benzoic acid**, $C_6H_4(COOH)_{(1)}(NH_2)_{(2)}$, is the type, are formed by reduction of the corresponding nitro-benzoic acids. Nitrous acid converts them into the corresponding oxyacids. Thus anthranilic acid yields salicylic acid. The o-acids exhibit a great tendency to the formation of lactams (p. 362), some of which are indigo derivatives, as **oxindole**, the lactam of o-amido-phenyl acetic acid, $C_6H_4\begin{cases}CH_2.CO_{(1)}\\ \quad\quad|\\ \quad NH_{(2)}\end{cases}$, and **dioxindole**, the lactam of o-amido-mandelic acid, $C_6H_4\begin{cases}CH(OH)CO_{(1)}\\ \quad\quad\quad|\\ \quad\quad NH_{(2)}\end{cases}$, (p. 411). Isatin, a product of oxidation of indigo, is the lactam of o-amido-benzoyl-formic acid, $C_6H_4\begin{cases}CO.CO_{(1)}\\ \quad|\\ NH_{(2)}\end{cases}$. The amido-cinnamic acids are closely related to quinolin (p. 468).

Phenyl-alanin (p. 364), is a phenyl-amido acid: β-phenyl-α-amido-propionic acid (formula above), which exists in certain lupines, and is a product of decomposition of the proteins. Its corresponding p-oxyphenyl derivative is

**Tyrosin** — p-Oxyphenyl alanin — $(HO)_{(4)}C_6H_4.CH_2.CH(NH_2).COOH$—one of the earliest known products of protein decomposition. Tyrosin is formed from proteins, particularly from casein, by the action of proteolytic enzymes, and during putrefaction, and is also formed from them by boiling with HCl or $H_2SO_4$, or by fusion with KHO, always accompanied by leucin (p. 364). It exists normally in the intestine, and pathologically in the urine (q. v.). It has been formed synthetically, from phenyl-acetaldehyde, $C_6H_5.CH_2.CHO$, by conversion into phenyl-alanin, $C_6H_5.CH_2.CH(NH_2).COOH$ and p-amido-phenyl-α-alanin, $C_6H_4(NH_2)_{(4)}.CH_2.CHNH_2.COOH$. It crystallizes in silky needles, arranged in stellate bundles, very sparingly soluble in cold water. soluble in 150 parts of hot water, more soluble

in the presence of acids or of alkalies, insoluble in alcohol and in ether. It unites with acids and bases to form salts. When heated it turns brown and gives off the odor of phenol; when heated to 270° (518° F.), it is decomposed into $CO_2$ and **oxyphenylethyl-amin**, $C_6H_4(OH).CH_2.CH_2.NH_2$, which sublimes.

With $H_2SO_4$, and slightly warmed, it dissolves with a transient red color; the solution, cooled, diluted, neutralized with $BaCO_3$, and filtered, gives a violet color with $Fe_2Cl_6$ (Piria's reaction). When moistened with $HNO_3$ and slowly evaporated, it leaves a yellow residue, which forms a deep reddish-yellow color with NaHO (Scherer's reaction). Heated with water and a few drops of Millon's reagent it gives a red liquid, and forms a red precipitate (Hofmann's reaction).

**p-Amidophenyl-α-alanin**—$NH_{2(4)}C_6H_4.CH_2.CH(NH_2).COOH$—produced by reduction of p-nitrophenyl-alanin, is both a phenyl-amido and an amido-phenyl acid.

**Anilido Acids** derived from the monocarboxylic acids are produced by the action of the monochlor-acids upon anilin, as the aliphatic amido-acids are obtained from ammonia (p. 362). Thus monochloracetic acid and anilin yield **anilido-acetic acid**, or **phenyl glycocoll**, $CH_2Cl.COOH+C_6H_5.NH_2=C_6H_5.NH.CH_2.COOH+HCl$.

**Hippuric Acid—Benzoyl-amido-acetic acid—Benzoyl glycocoll**—$C_6H_5.CO.NH.CH_2.COOH$—is similarly obtained from monochloracetic acid and benzamid: $CH_2Cl.COOH+C_6H_5.CO.NH_2=C_6H_5.CO.NH.CH_2.COOH+HCl$. It is also formed by the action of benzoyl chlorid upon glycocoll in the presence of sodium hydroxid: $CH_2(NH_2).COOH+C_6H_5.CO.Cl=C_6H_5.CO.CH_2.NH.COOH+HCl$. Hippuric acid exists in the urine of the herbivora; and in human urine in the daily quantity of 0.29–2.84 grams, and in larger amount when benzoic acid, cinnamic acid and other aromatic substances are taken. It crystallizes in prisms, colorless, odorless, bitter, sparingly soluble in water, readily soluble in alcohol, fuses at 187° (368.6° F.). When heated with acids or alkalies it is decomposed into benzoic acid and glycocoll. Oxidizing agents convert it into benzoic acid, benzamid and carbon dioxid. When heated alone it gives off a sublimate of benzoic acid and the odor of hydrocyanic acid. Its ferric salt is insoluble, and is formed as a brown precipitate when $Fe_2Cl_6$ is added to its solution. Heated with lime it forms benzene and ammonia.

**Anilic Acids** are anilido acids corresponding to the dicarboxylic acids. They may be considered as being formed by substitution of the univalent remainder of the acid for H in anilin, and therefore as anilids (p. 421); or by substitution of phenyl for H in the $NH_2$ group of the amic acids (pp. 346, 361). Thus **oxanilic acid**, $C_6H_5.NH.CO.COOH$, corresponds to oxalic acid, COOH.COOH, and to oxamic acid, $CONH_2.COOH$.

**Carbanilic Acid**—$O:C\langle^{OH}_{NH.C_6H_5}$—the anilic acid corresponding to carbonic and carbamic acids, and isomeric with phenyl urethan (p. 347), is not known in the free state. Its esters, however, are known as phenyl urethans. A great number of phenyl-urea and phenyl-guanidin derivatives are also known.

Related to the amido acids are the hydroxamic acids and the anil acids.

**Hydroxamic Acids** are derivable from the imid formula of benzamid (p. 423) by substitution of OH for H in the imid group. Thus benzhydroxamic acid, $C_6H_5.C\langle^{NOH}_{OH}$, corresponds to benzamid, $C_6H_5.C\langle^{NH}_{OH}$. Both H atoms in the OH groups are replaceable by alkyls to form esters. **Amidoxims** (p. 335) are derived from the hydroxamic acids by substitution of $NH_2$ for OH, e. g., benzenyl-amidoxim, $C_6H_5.C\langle^{NOH}_{NH_2}$.

**Anil Acids** are anilin derivatives of the ketone-carboxylic acids (p. 298), formed by the union of anilin and the acid, with elimination of water. Thus anilin and pyroracemic acid yield anil-pyroracemic acid: $C_6H_5.NH_2+CH_3.CO.COOH=H_2O+C_6H_5.N:C(CH_3).COOH$.

### DIAZO, DIAZOAMIDO, AND AZO COMPOUNDS.

Diazo compounds contain the group —N:N—, united by one bond to an aromatic group, and by the other to an acid radical.

Diazoamido compounds contain the group —N:N.NH—, united to two aromatic groups.

Azo compounds contain the group —N:N—, united to two aromatic hydrocarbon groups, or to one aromatic and one aliphatic hydrocarbon group. The derivatives of each of the classes are produced by substitution for hydrogen.

**Diazo Compounds**—**Diazobenzene**, $C_6H_5.N:N.H$, does not exist free; and the diazo compounds in general readily undergo decomposition, and are hence largely used in the preparation of a variety of substitution products, and notably in the manufacture of a great number of azo-dyes, to which class most of the so-called anilin dyes belong.

The diazo compounds are produced by the action of nitrous acid upon the corresponding anilin compounds. Thus anilin hydrochlorid with $HNO_2$ forms diazobenzene chlorid: $C_6H_5.NH_3Cl+HNO_2=C_6H_5.N:N.Cl+2H_2O$. The reaction must be conducted at a low temperature, otherwise the anilin compound will suffer the same decomposition by $HNO_2$ as do its congeners, the primary aliphatic amins (p.

328); i. e., the N is eliminated, and a phenol, water and the acid are formed: $C_6H_5.NH_3Cl+HNO_2=C_6H_5.OH+N_2+H_2O+HCl$.

The diazo compounds are mostly crystalline solids, colorless when pure, but turning brown in air, readily soluble in water, sparingly soluble in alcohol, insoluble in ether, and decomposing explosively when heated or struck. Their N is readily displaced by H, OH, or the halogens or cyanogen, with formation of hydrocarbons, phenols, haloids, and cyanids, and regeneration of the acid. Thus diazobenzene sulfate yields phenol by hydration: $C_6H_5.N:N.HSO_4+H_2O=C_6H_5.OH+N_2+H_2SO_4$.

By reduction they form hydrazins. Thus potassium diazobenzene sulfonate forms potassium benzene-hydrazin sulfonate: $C_6H_5.N:N.SO_3K+H_2=C_6H_5.HN.NH.SO_3K$.

Heated with aromatic amins or phenols, they form amido- or hydroxyl azo compounds, which, either in their own form or in those of their sulfonic acids or salts, are the azo dyes.

**Diazoamido and Disdiazoamido Compounds.**—The diazoamido compounds, containing the group —N:N.NH— united to two aromatic groups, are formed by the action upon each other of diazo salts and primary or secondary amins in equal molecular proportion. Thus diazoamido benzene, $C_6H_5.N:N.NH.C_6H_5$, is formed, as a yellow, crystalline, explosive solid, insoluble in water, soluble in hot alcohol, by the action of diazobenzene nitrate, or chlorid, upon anilin: $C_6H_5.N:NCl+NH_2.C_6H_5=C_6H_5.N:N.NH.C_6H_5+HCl$.

The most notable property of these substances is their transformation, by intramolecular rearrangement, into the isomeric p-azo-amido compounds. Thus diazoamido benzene becomes p-azo-amido benzene, $C_6H_5N:NC_6H_4.(NH_2)_{(4)}$. This intramolecular transposition takes place slowly in the presence of traces of anilin salts, at the ordinary temperature.

The **disdiazoamido** compounds, containing the group —N:N.NH.N:N—, are formed under the same conditions as the diazoamido compounds, except that two molecules of the diazo salt are taken for one of the amin: $2C_6H_5.N:NCl+NH_2.C_6H_5=C_6H_5.N:N.N(C_6H_5).N:N.C_6H_5+2HCl$.

**Azo Compounds.**—The azo compounds contain the same group, —N:N—, as the diazo compounds, but they differ from the latter in that the two valences are both satisfied by hydrocarbon groups; either both aromatic, as in **azobenzene**, $C_6H_5.N:N.C_6H_5$, or one aromatic and one aliphatic, as in **benzene azo-methane**, $C_6H_5.N:N.CH_3$. They are "mixed," "symmetric," and "unsymmetric," according as they contain an aromatic and an aliphatic group, or two like aromatic groups, or two unlike aromatic groups. In designating the orientation of substituted groups the —N:N— attachments are con-

sidered as occupying the (1) position in both hydrocarbon groups, and the positions of substitution in one ring are indicated by 2, 3, etc., and those in the other by 2′, 3′, etc.

The azo compounds are formed: (1) By moderate reduction of nitro-aromatic compounds in alkaline solution. The reaction takes place in two stages, an azoxy compound being first formed and then further reduced. Thus nitro-benzene forms, first azoxybenzene, then azobenzene: $2C_6H_5.NO_2+3H_2=C_6H_5.N\overset{O}{\diagup\!\diagdown}N.C_6H_5+3H_2O$, and then $C_6H_5.N\overset{O}{\diagup\!\diagdown}N.C_6H_5+H_2=C_6H_5.N:N.C_6H_5+H_2O$. The reduction readily progresses further, and always does so in acid solutions, with formation, first of a hydrazo product (below), and finally an amido derivative (pp. 417, 419). Thus azobenzene forms, first, hydrazobenzene, or symmetrical diphenyl hydrazin, and then anilin: $C_6H_5.N:N.C_6H_5+H_2=C_6H_5.NH.NH.C_6H_5$, and $C_6H_5.NH.NH.C_6H_5+H_2=2C_6H_5.NH_2$. (2) By reduction of the azoxy compounds. (3) The amido derivatives of the azo hydrocarbons are technically manufactured by molecular rearrangement of the diazoamido compounds (p. 427), or (4) by acting upon the tertiary anilins, or upon the m-diamins, with diazo salts.

The azo compounds are much more stable than the diazo compounds. The hydrocarbons, such as azobenzene, $C_6H_5.N:N.C_6H_5$, are highly colored crystalline solids, which are not basic, and do not act as dyes. They are sparingly soluble in water, readily soluble in alcohol and in ether. Their most important derivatives are the amido-azo compounds, which are highly colored and strongly basic, crystalline solids, whose solutions have, however, no dyeing power. But they combine readily with salt-forming groups, notably to form sulfonic acids, which constitute many of the most extensively used "anilin dyes."

p-Amido-azobenzene — $C_6H_5.N:N.(C_6H_4)(NH_2)_{(4)}$ — prepared by the methods given above, is the starting point in the manufacture of several yellow, orange, and brown "diazo dyes," and of the "inuline dyes." It forms yellow needles, fusing at 123° (253.4° F.).

### HYDRAZIN COMPOUNDS.

The aromatic hydrazins are derived from the hypothetical diamid, $H_2N.NH_2$ (p. 105), by substitution of hydrocarbon or other aromatic radicals for one or more of the hydrogen atoms (p. 337).

Hydrazo-benzene — sym. Diphenyl-hydrazin — $C_6H_5.NH.NH.C_6H_5$—is obtained by moderate reduction, as with zinc dust or sodium amalgam, of azobenzene: $C_6H_5.N:N.C_6H_5+H_2=C_6H_5.NH.NH.C_6H_5$.

It forms colorless crystals, having the odor of camphor, fusible at 132° (267.8° F.), insoluble in water, soluble in alcohol and in ether. It readily oxidizes to azobenzene. Strong reducing agents break it up into two molecules of anilin. It is not basic; but, when treated with strong acids, it suffers molecular rearrangement, with formation of **benzidin**, or **p(2)-diamido-diphenyl** (p. 447), $NH_{2(4)}.C_6H_4.C_6H_4.NH_{2(4)}$.

The **unsymmetrical hydrazins** resemble each other in their properties and methods of formation, but differ from the symmetrical compounds, notably in that, containing the $-NH.NH_2$ group, they are monacid bases, forming salts corresponding to those of ammonia and the amins.

**Phenylhydrazin**—$C_6H_5.NH.NH_2$—is formed by reduction of the diazo salts, of the diazo-amido compounds, or of the nitroso-amins. Thus stannous chlorid and diazobenzene chlorid yield phenylhydrazin hydrochlorid: $C_6H_5N:NCl + 2SnCl_2 + 4HCl = C_6H_5.NH.NH_3Cl + 2SnCl_4$. Zinc dust and acetic acid decompose diazoamido-benzene into phenylhydrazin and anilin: $C_6H_5.N:N.NH.C_6H_5 + 2H_2 = C_6H_5.NH.NH_2 + NH_2.C_6H_5$.

Phenylhydrazin is a yellow oil, which crystallizes at 23° (73.4° F.), and boils at 242° (467.6° F.) with partial decomposition, or at 120° (248° F.), without decomposition, under 12 mm. pressure. It reduces Fehling's solution, or when boiled with $CuSO_4$ it liberates nitrogen and forms benzene. Sodium displaces the imid H to form α sodium phenylhydrazin: $C_6H_5.NaN.NH_2$. The alkyl haloids cause substitution of alkyls for both amid and imid H, forming α and β **phenylalkyl hydrazins.** One of the latter, **β methyl-phenylhydrazin,** $C_6H_5.NH.NH.CH_3$, is an intermediate product in the formation of antipyrin from phenylhydrazin. Heated to 200° (392° F.) with fuming HCl, phenylhydrazin is converted into **p-phenylene-diamin:** $C_6H_5.NH.NH_2 = NH_2.C_6H_4.NH_2$.

**Phenyl-hydrazones** and **Osazones.**—A most important action of phenylhydrazin is that with aldehydes and ketones, and with aldo- and keto-alcohols, and aldehyde and ketone acids and their esters, in which the bivalent remainder $=N.NH.C_6H_5$ takes the place of oxygen in the aldehyde or ketone group, with the formation of **phenyl-hydrazones** and **osazones,** in much the same manner as the aldoxims and ketoxims are formed from the aldehydes and ketones (pp. 360, 361). The formation of these derivatives is utilized to identify the aldehydes and ketones and, notably, the aldoses and ketoses (p. 264, also "phenylhydrazin reaction").

The phenyl-hydrazones and osazones are formed by a variety of methods, usually by heating the aldehyde or ketone compound with phenylhydrazin hydrochlorid in presence of sodium acetate. In the

formation of the aldehydrazones and ketohydrazones the reaction takes place with elimination of water according to the equations: $CH_3.CH_2.CHO + H_2N.NH.C_6H_5 = CH_3.CH_2.CH:N.NH.C_6H_5 + H_2O$, and $CH_3.CO.CH_3 + H_2N.NH.C_6H_5 = CH_3.C:(N.NH.C_6H_5).CH_3 + H_2O$.

In the formation of the osazones of the aldoses and ketoses two molecules of phenylhydrazin react with one of the sugar, with elimination of water. In the first stage of the reaction a hydrazone is formed as with the aldehydes and ketones. Thus with glucose and fructose respectively (pp. 268, 269):

$$\begin{array}{l} CHO \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{array} + H_2N.NH.C_6H_5 = \begin{array}{l} CH:N.NH.C_6H_5 \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{array} + H_2O, \text{ and}$$

$$\begin{array}{l} CH_2OH \\ | \\ CO \\ | \\ (CHOH)_3 \\ | \\ CH_2OH \end{array} + H_2N.NH.C_6H_5 = \begin{array}{l} CH_2OH \\ | \\ C:N.NH.C_6H_5 \\ | \\ (CHOH)_3 \\ | \\ CH_2OH \end{array} + H_2O;$$

The CHOH or $CH_2OH$ group vicinal to the first substitution then becomes oxidized to CO or CHO, and a second $=N.NH.C_6H_5$ group is substituted for the O to form the osazone:

$$\begin{array}{l} CH:N.NH.C_6H_5 \\ | \\ CO \\ | \\ (CHOH)_3 \\ | \\ CH_2OH \end{array} + H_2N.NH.C_6H_5 = \begin{array}{l} CH:N.NH.C_6H_5 \\ | \\ C:N.NH.C_6H_5 \\ | \\ (CHOH)_3 \\ | \\ CH_2OH \end{array} + H_2O, \text{ and}$$

$$\begin{array}{l} CHO \\ | \\ C:N.NH.C_6H_5 \\ | \\ (CHOH)_3 \\ | \\ CH_2OH \end{array} + H_2N.NH.C_6H_5 = \begin{array}{l} CH:N.NH.C_6H_5 \\ | \\ C:N.NH.C_6H_5 \\ | \\ (CHOH)_3 \\ | \\ CH_2OH \end{array} + H_2O.$$

A comparison of the above formulæ will indicate why it is that glucose and fructose yield one and the same osazone.

The phenyl-hydrazones are also utilized in the formation of condensed heterocyclic compounds. Thus acetone phenyl hydrazone, $\begin{array}{l} CH_3.C:N.NH.C_6H_5 \\ | \\ CH_3 \end{array}$ is converted into a methyl indole (p. 464), $\begin{array}{l} CH_3.C.NH \\ \| \quad \diagdown \\ CH \quad \diagup \end{array} C_6H_4$, by loss of $NH_3$.

**Acid Derivatives of Phenylhydrazin.**—A great number of compounds are known, formed by the substitution of acid radicals for

the amid or imid hydrogen of phenylhydrazin. These compounds bear the same relation to phenylhydrazin that the anilids bear to anilin, and some of them have been used as antipyretics, e. g., **β acetophenyl-hydrazid — Hydracetin** — $C_6H_5.NH.NH.CO.CH_3$ — formed as a white, crystalline, tasteless, and odorless powder, sparingly soluble in water, by the action of acetyl chlorid or of acetic anhydrid upon phenylhydrazin. It is the active ingredient of an antipyretic called **pyrodin.**

## B. HYDROAROMATIC COMPOUNDS WITH A SINGLE NUCLEUS.

The hydroaromatic compounds may be considered as derived from the benzenic by rupture of one or more of the double linkages of the benzene ring (p. 380), by which the valence of the nucleus is changed from six to eight, ten or twelve.

### HYDROCARBONS.

**Hexahydrobenzenes —Cyclohexanes—Naphthenes.**—These compounds, of which **hexahydrobenzene,** $H_2C\langle^{CH_2.CH_2}_{CH_2.CH_2}\rangle CH_2$, is the simplest, and the parent substance of the hydroaromatic compounds, exist in Russian petroleum, in coal tar, and in "rosin-oils." They are isomeric with the olefins, from which they may be distinguished by the fact that they do not combine with bromin.

**Tetrahydrobenzenes — Cyclohexenes —Naphthylenes**— of which the lowest term is **tetrahydrobenzene,** $H_2C\langle^{CH_2.CH}_{CH_2.CH_2}\rangle CH$, exist in rosin-oils.

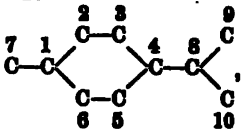
**Dihydrobenzenes—Cyclohexadiënes**—of which the first member is **dihydrobenzene,** $HC\langle^{CH.CH_2}_{CH_2.CH}\rangle CH$, probably exist in many of the natural products called

**Terpenes.**—Most of the volatile, or essential oils, or essences, obtained by distillation of various plants with steam, consist of hydrocarbons having the formula $C_{10}H_{16}$, and most of the camphors and resins are alcoholic or ketonic derivatives of these hydrocarbons. A few of the essential oils, having the formula $C_5H_8$, are known as **hemiterpenes,** or **olefin terpenes,** and are unsaturated aliphatic compounds (p. 371). Some of the aromatic terpenes also are polymeres, having the formulæ $x(C_5H_8)$. Although the constitution of the aromatic terpenes is not completely established, they are hydroaromatic hydrocarbons of which the camphors are alcohols or ketones.

The terpenes form benzenic compounds by oxidation. With the halogens they form addition products, which not only serve for their classification, but also for their conversion into alcohol-camphors. With nitrosyl chlorid, NOCl, they form well-defined nitroso-chlorids, as dipentene nitroso-chlorid, $C_{10}H_{16}(NO)Cl$, which serve for their identification, and for the preparation of basic and other derivatives.

The true terpenes and their derivatives are arranged in two classes: (1) The *Terpan group*, and (2) the *Camphan group*.

The terpans are capable of taking on four bromin atoms, and therefore have two double linkages. It is assumed that in them the ten carbon atoms are arranged in a hexacarbon ring, with two lateral chains in the p- position to each other, thus:




and that two of the ten bonds are double. The hydrocarbons are, therefore, dihydrocymenes (p. 387). The carbon atoms are numbered as above to indicate the positions of the double linkages, which vary in the different isomeres. The positions of double linkage are marked by the Greek capital $\Delta$, followed by the numbers of the carbon atoms from which the attachment proceeds:

Limonene—$\Delta_{(1,8)}$Dihydrocymene—$CH_3.C\langle{CH\ CH_2 \atop CH_2CH_2}\rangle C^*H.C\langle{CH_2 \atop CH_3}$—

(probably) exists in three optical isomeres: d-limonene; b. p. 175° (347° F.); $[a]_D = +106.8°$; a liquid having the odor of lemons, existing in many essential oils, such as those of orange, bergamot, dill, etc.: l-limonene; b. p. 175° (347° F.); $[a]_D = -105°$; occurs in the oils of peppermint, fir and pine needles. [d+l]-limonene, dipentene, or cinene; b. p. 175° (347° F.); occurs in oil of wormseed, and is produced by the action of a heat of 250°–300° upon limonenes, pinene and camphene, and therefore exists in turpentine oil produced at high temperatures, such as the Russian and Swedish. The limonenes are liquids having the odor of lemons, and combining with bromin to produce solid tetrabromids having the same optical action as the parent hydrocarbons.

Other terpans are: Terpinolene; f. p. 75°; formed when terpin hydrate, terpineol, or cineol is heated with dilute $H_2SO_4$, or by the action of the concentrated acid on pinene. Sylvestrene; b. p. 176°; $[a]_D = +66.32°$; occurs in Swedish and Russian turpentine. Terpinene; b. p. 180°; is formed when dipentene, terpin, phellandrene, terpineol or cineol is heated for some time with dilute alcoholic $H_2SO_4$, or by the action of the concentrated acid on pinene, or by the action of formic acid on linalool (p. 372). It is not converted into other terpans by acids, and does not yield a bromin derivative,

but forms a nitroso-chlorid. **Phellandrene**; b. p. 170°; exists in d- and l-modifications. It has the same negative qualities as terpinene. **Menthene**, $C_{10}H_{18}$, is a hydroterpan, formed by acting upon potassium phenate with menthyl chlorid; b. p. 167°.

The members of the **camphan group** are capable of taking up two bromin atoms, and are considered as probably containing a dihydrobenzene ring with a $-\overset{CH_3}{\underset{CH_3}{C}}-$ group linking the p-positions internally, as in the probable formula of

**Camphene** — $CH_3—C\overset{CH_2—CH_2}{(CH_3.C.CH_3)}—CH$—which is a solid; f. p. 43° (109.4° F.); b. p. 160° (320° F.); $n_D = 1.45514$ (54°); (p. 21); known in d-, l-, and [d+l] modifications. It exists in Ceylon citronella oil, and is produced by the action of dehydrating agents upon its alcohol, Borneo-camphor (p. 435). It forms a dibromid.

**Pinene** — $C_{10}H_{16}$ — is the principal constituent of oil, or essence of turpentine, and exists also in many other essential oils. It is a colorless liquid; b. p. 155° (311° F.); sp. gr. 0.858 (20°); $n_D =$ 1.46553 (21°). It exists in three optical isomeres: **d-pinene**; $[a]_D = 17°$; predominates in American oil of turpentine; **l-pinene**; $[a]_D = -40.3°$; in the French oil. Pinene combines with bromin to form a **dibromid**: it, therefore, contains one double linkage. When dry HCl gas is passed through pinene, well cooled, a white, crystalline substance, fusing at 125° (257° F.), and having the odor of camphor, separates. This is **d-pinene hydrochlorid**, $C_{10}H_{17}Cl$, or "artificial camphor."

**Turpentine** is a yellowish-white, semi-solid substance, having a balsamic odor, which exudes from incisions in the bark of *Pinus palustris*, *P. tæda*, and other *Coniferæ*, and which may be taken as the type of a number of other similar products. These substances, when distilled with steam, yield two products, one a solid, yellow or brown residue, a **stearoptene**, such as **rosin** or **colophany**; the other a volatile, oily liquid, an **eleoptene**, such as **oil, or essence, of turpentine.** Oil of turpentine is insoluble in water, mixes with alcohol and with ether, and dissolves phosphorus, sulfur and caoutchouc. When exposed to the air it is oxidized to gummy, aldehydal products, which finally harden, hence its use as a drier in the manufacture of paints and varnishes. On contact with $HNO_3$, its oxidation is so violent as to cause ignition. $H_2SO_4$ also acts upon it energetically, with formation of a number of polymeres.

**Hydroterpenes** are naphthenes (p. 431) obtained by decomposition of certain natural alcohol-camphors. Thus **hexahydrocymene**, $H_3C.CH\langle^{CH_2.CH_2}_{CH_2.CH_2}\rangle CH.CH\langle^{CH_3}_{CH_3}$, is derived from menthol (p. 435).

## HYDROAROMATIC ALCOHOLS.

The hydroaromatic alcohols are, for the most part, "ring alcohols," and contain either CHOH or COH, as a part of the ring, although in some, as in some of the terpan alcohols (below), the alcoholic group, which may then also be $CH_2OH$, is contained in the lateral chain. These alcohols may be obtained by reduction of the corresponding ketones (p. 436), or of other aromatic or hydroaromatic compounds. Several of them, such as quercite, inosite and some of the camphors, are natural products.

**Quinite** — $HOHC\langle^{CH_2.CH_2}_{CH_2.CH_2}\rangle CHOH$ — and **phloroglucite** — $HOHC\langle^{CH_2.CHOH}_{CH_2.CHOH}\rangle CH_2$ — are reduction products of the phenols, quinol, $HOC\langle^{CH:CH}_{CH.CH}\rangle COH$, and phloroglucin, $HOC\langle^{CH:COH}_{CH.COH}\rangle CH$ respectively (p. 394).

**Quercite** — $H_2C\langle^{CHOH.CHOH}_{CHOH.CHOH}\rangle CHOH$ — a pentatomic alcohol, obtained from acorns. It is a sugar-like substance, but is not affected by alkalies, does not ferment, and does not reduce Fehling's solution. F. p. 235°; $[\alpha]_D = +24.16°$.

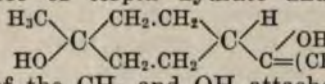
**Inosite** — $C_6H_5(OH)_6$ — metameric, though not related, to the glucoses, is a hexatomic alcohol, in which probably two hydroxyls are attached to the same carbon atom, as it exists in three optical modifications. The inactive modification exists in the liquid of muscular tissue, in the lungs, kidneys, liver, spleen, brain and blood; in traces in normal urine, and increased in Bright's disease, in diabetes, and after the use of drastics in uræmia; in the contents of hydatid cysts; in beans and peas, and in certain other seeds and leaves. It crystallizes in needles, usually arranged in cauliflower-like masses, has a sweet taste, is readily soluble in water, sparingly soluble in alcohol, insoluble in absolute alcohol and in ether. It does not ferment, is not colored by alkalies, and does not reduce Fehling's solution. When heated to 170° (338° F.) with HI, it is decomposed into phenol, diiodophenol and benzene. When treated with $HNO_3$, evaporated to near dryness, the residue moistened with $NH_4HO$ and $CaCl_2$, and again evaporated, a rose-red residue is left (Scherer's reaction). Mercuric nitrate produces in solutions of inosite a yellow precipitate, which, on cautious heating, turns red. The color disappears on cooling and reappears on heating (Gallois' reaction).

**Dambonite**, a supposed glucosid (p. 409) obtained from an African caoutchouc, is the dimethyl ether of i-inosite (dambose).

The terpan alcohols are derivatives of hexahydrocymene, or menthan (p. 433), $H_3C.CH\langle^{CH_2.CH_2}_{CH_2.CH_2}\rangle CH.CH\langle^{CH_3}_{CH_3}$, or $C_{10}H_{20}$; or of menthene, $C_{10}H_{18}$; or of menthadiene, $C_{10}H_{16}$; differing from menthan

by the introduction of one and two double bonds respectively. They are monacid, diacid, etc., according to the number of hydroxyls substituted for hydrogen. Among them are menthol and terpin and its hydrate.

**Menthol — Oxyhexahydrocymene** — $H_3C.CH\langle^{CH_2.CH(OH)}_{CH_2.CH_2}\rangle CH..CH\langle^{CH_3}_{CH_3}$ — is a monacid menthan alcohol. It is the chief constituent of oil of peppermint. It crystallizes in prisms, fusible at 42° (107.6° F.), sparingly soluble in water, readily soluble in alcohol, ether and carbon disulfid, and in acids. Corresponding to it are a series of menthyl esters.

**Terpins.**—There are two diacid **menthan alcohols,** in which the hydroxyls occupy the 1,8 positions (p. 432). The formula of **cis-terpin,** the parent substance of terpin hydrate and of cineol, is now considered as being  , while in **trans-terpin** the positions of the $CH_3$ and OH attached to C(1) are reversed. Cis-terpin is obtained by dehydration of terpin hydrate, and also from [d+l]-limonene dihydrochlorid (p. 432). It is crystalline, fuses at 104° (219.2° F.), and boils at 258° (496.4° F.). It absorbs water eagerly to form terpin hydrate. Gaseous HCl, or $PCl_3$, converts it into [d+l]-limonene hydrochlorid.

**Terpin Hydrate** — $C_{10}H_{18}(OH)_2 + H_2O$ — is formed when oil of turpentine remains long in contact with water, more rapidly in presence of alcohol and dilute $HNO_3$; also, similarly, from pinene and from limonene. It forms rhombic crystals, fusible at 117° (242.6° F.), with loss of $H_2O$ and conversion, slowly, into terpin. It is easily soluble in alcohol, sparingly soluble in water, chloroform and ether. It is used as an expectorant.

**Cineol — Eucalyptol** — $C_{10}H_{16}(OH)_2$ — another diacid menthan alcohol, is obtained from the leaves of *Eucalyptus globulus*, and also exists in wormseed oil (*Oleum cinæ*) and in other volatile oils. It is a colorless oil, having a camphor-like odor; sp. gr. 0.93 at 15°; b. p. 176°; $n_D = 1.4559$; soluble in alcohol, sparingly soluble in water. Dry HCl gas passed through its petroleum ether solution separates white scales of **eucalypteol,** $C_{10}H_{16}.2HCl$, which is decomposed by water with regeneration of cineol.

**Terpineols** are monacid **menthene alcohols.** The $\Delta_1$, $(OH)_{(8)}$ terpineol is formed by removal of $2H_2O$ from terpin hydrate. It is a solid; f. p. 35° (95° F.). When boiled with dilute acids it forms carvacrol (p. 392), and the ketone, carvone (p. 436). It forms dipentene when heated with $KHSO_4$.

**Borneol — Camphol — Borneo Camphor**—$C_{10}H_{18}O$ — a monacid alcohol, is the best known of the **camphan alcohols.** It exists in

three optical modifications; the d-borneol being the one usually met with, and obtained from *Dryobalanops camphora*. The d- and l-modifications are both formed by hydrogenation of laurel camphor. It forms small, friable crystals; has an odor recalling those of laurel camphor and of pepper, and a hot taste; is insoluble in water, readily soluble in alcohol, ether, and acetic acid; fuses at 203° (397.4° F.); boils at 212° (413.6° F.). It is oxidized to laurel camphor by $HNO_3$. Heated with $KHSO_4$, it is decomposed into camphene (p. 433) and $H_2O$.

### HYDROAROMATIC KETONES AND ACIDS.

The hydroaromatic ketones are "ring ketones," the CO group forming a part of the ring. They are formed: (1) by reduction of the corresponding aromatic phenols; (2) by oxidation of the secondary ring-alcohols; (3) by condensation of the esters of the aliphatic ketone acids (p. 298), or of the ketones. The terpan and camphan ketones exist in nature. The ketones form ketoxims with hydroxylamin (p. 361), and hydrazones with phenyl hydrazin (p. 429), which serve for their identification.

Pimelin-ketone—$CH_2\begin{cases}CH_2.CH_2\\CH_2.CH_2\end{cases}CO$—is the simplest of the hydroaromatic ketones. It is an oil, having the odor of peppermint; b. p. 155°; formed by electrolytic reduction of phenol; by oxidation of hexahydrophenol, $CH_2\begin{cases}CH_2.CH_2\\CH_2.CH_2\end{cases}CHOH$; or by distillation of calcium pimelate, $CH_2\begin{cases}CH_2.CH_2.CO_2\\CH_2.CH_2.CO_2\end{cases}Ca$ (p. 289). Its oxim fuses at 88°.

The terpan ketones, or ketohydro-p-cymenes, are formed by oxidation of the corresponding secondary alcohols (p. 435).

Menthone—$C_{10}H_{18}O$—(CO–3)—is a ketomenthan, existing in oil of peppermint. It is known in two optical isomeres: l-menthone is formed by oxidizing menthol, and is converted into d-menthone by contact with $H_2SO_4$. B. p. 206°; $[a]_D = -28°$ and $+28°$. l-Menthoxim fuses at 59°.

Thujone—Tanacetone—and Pulegone—$C_{10}H_{16}O$, are ketomenthenes, the former, b. p. 200°, existing in tansy and thuja oils; the latter, b. p. 221°, in "polei-oils."

Carvone—Carvol—$C_{10}H_{14}O$—is a ketomenthadiëne, known in three optical isomeres, which boil at 225°. d-Carvol exists in cumin and dill oils; $[a]_D = +62°$. Heated with KHO, it is converted into its isomere carvacrol (p. 392). The three carvoxims are formed either by the action of hydroxylamin upon the corresponding carvones, or by the action of boiling KHO upon the three limonene nitrosochlorids (p. 432).

d-Camphor—Common camphor—Laurel camphor—Japan cam-

**phor**—$C_{10}H_{16}O$—is the most important of the **camphan ketones.** It is obtained from the camphor tree (*Laurus camphora*), and is formed artificially by oxidation of borneol or of camphene. It forms translucent, friable crystals; hot and bitter in taste, aromatic; sparingly soluble in water, quite soluble in acetic acid, methylic and ethylic alcohols, and the oils; f. p. 175° (347° F.); b. p. 204° (399.2° F.); sp. gr. 0.985; sublimes at all temperatures; $[a]_D = +44.22$.

It ignites readily, and burns with a luminous flame. Cold $HNO_3$ dissolves it, and $H_2O$ precipitates it unchanged from the solution. Hot $HNO_3$, or potassium permanganate, oxidizes it to d-camphoric acid. Distilled with $P_2O_5$ it yields cymene, $C_{10}H_{14}$. Reducing agents convert it into borneol. Heated with iodin, it is converted into carvacrol (p. 392). Bromin unites with it to form ruby-red crystals of an unstable compound, $C_{10}H_{14}OBr_2$, which, when heated, fuse and give off HBr, leaving an amber-colored residue, which, on recrystallization from boiling alcohol, leaves long, hard, rectangular crystals of **monobromo-camphor,** $C_{10}H_{15}OBr$; f. p. 76°; soluble in alcohol and in ether.

**l-Camphor** is obtained from the oil of *Matricaria postlantum;* $[a]_D = -44.22°$. **[d + l]-Camphor** exists in the essential oils of rosemary, sage, lavender and origanum, or is formed by mixing d- and l- camphors, or by oxidation of [d+l]-borneol, or of [d+l]-camphene. F. p. 179°.

**Hydroaromatic Carboxylic Acids.**—A great number of these acids are known, some pure acids, others oxy- or ketonic acids, containing from one to six carboxyl groups, and hexahydro-, tetrahydro- and dihydro-. The most important are:

**Quinic Acid — Hexahydro-tetraoxybenzoic Acid** — $C_6H_7(OH)_4.COOH$ — which exists, combined with the alkaloids, in cinchona barks, also in coffee beans and in other plants. It forms hard, transparent prisms, soluble in water and in alcohol; fuses at 160°; lævogyrous. On distillation, it yields phenol, hydroquinol, benzoic acid and salicylic aldehyde. Hydriodic acid reduces it to benzoic acid.

**Terebic Acid** — $C_7H_{10}O_4$ — f. p. 175°; and **Terpenylic Acid** — $C_8H_{12}O_4$ — f. p. 90°, are oxidation products of oil of turpentine, obtained, the former with $HNO_3$, the latter with chromic acid mixture.

**Camphoric Acids**—$C_8H_{14}(COOH)_2$.—The d-, l-, and [d+l]-acids are known. **d-Camphoric acid** is produced by oxidizing common d-camphor by heating with $HNO_3$. It forms colorless, odorless needles, soluble in alcohol, ether and boiling water; f. p. 187°; $[a]_D = +49.7°$. By further oxidation it yields camphoronic acid, or trimethyl-tricarballylic acid (p. 289).

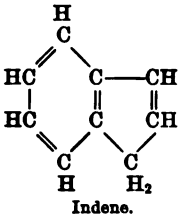
**Resins**—are generally the products of oxidation of the hydrocarbons allied to pinene; are amorphous (rarely crystalline); insol-

uble in water; soluble in alcohol, ether, and essences. Many of them contain acids.

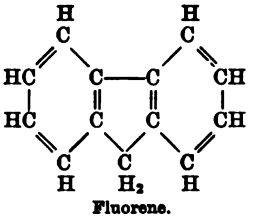
They may be divided into several groups, according to the nature of their constituents: (1) **Balsams**, which are usually soft or liquid, and are distinguished by containing free cinnamic or benzoic acid (q. v.). The principal members of this group are *benzoin*, *liquid-ambar*, *Peru balsam*, *styrax*, and *balsam tolu*; (2) **oleo-resins** consist of a true resin mixed with an oil, and usually with an oxidized product other than cinnamic or benzoic acid. The principal members of this group are *Burgundy* and *Canada pitch*, *Mecca balsam*, and the resins of *capsicum*, *copaiva*, *cubebs*, *elemi*, *labdanum*, and *lupulin*; (3) **gum-resins** are mixtures of true resins and gums. Many of them are possessed of medicinal qualities: *aloes*, *ammoniac*, *asafœtida*, *bdellium*, *euphorbium*, *galbanum*, *gamboge*, *guaiac*, *myrrh*, *olibanum*, *opoponax*, and *scammony*; (4) **true resins** are hard substances obtainable from the members of the three previous classes, and containing neither essences, gums, nor aromatic acids. Such are *colophony* or *rosin*, *copal*, *dammar*, *dragon's blood*, *jalap*, *lac*, *mastic*, and *sandarac*; (5) **fossil resins**, such as *amber*, *asphalt*, and *ozocerite*.

## C. COMPOUNDS WITH CONDENSED NUCLEI.

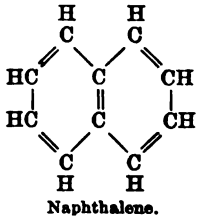
These compounds contain two or more benzene rings, or one or more benzene rings and a pentacarbocyclic ring, fused together in such manner that the adjacent rings have two carbon atoms in common. The parent hydrocarbons of these compounds are: indene, fluorene, naphthalene, anthracene, phenanthrene, chrysene, and picene:



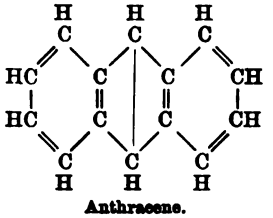
Indene.



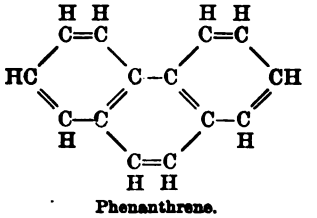
Fluorene.



Naphthalene.



Anthracene.



Phenanthrene.

The derivatives of these hydrocarbons are similar in their general properties to the benzene derivatives, with some differences in orientation. Chrysene, $C_{18}H_{12}$, and picene, $C_{22}H_{14}$, are naphthalene-phenanthrenes (p. 441). Most of these hydrocarbons form crystalline addition products with picric acid.

## CONDENSED HYDROCARBONS.

These hydrocarbons accompany benzene in coal-tar. Naphthalene and anthracene are obtained from this source industrially.

**Indene**—$C_9H_8$—(constitution, p. 438)—exists in the fraction of coal-tar, distilling between 176° and 182°. It has also been obtained synthetically. Indene derivatives can also be produced from naphthalene derivatives, one benzene ring being converted into a pentacarbocyclic ring (see formulæ, p. 438). Indene is the hydrocarbon corresponding to indole, which contains NH in place of the $CH_2$ group (p. 463). It is an oil; b. p. 178°; sp. gr. 1.04 at 15°. At a red heat two molecules of indene unite, with loss of 4H, to form chrysene (p. 441). By reduction indene is converted into **hydrindene**, $C_6H_4$:$(CH_2)_3$; an oil; b. p. 177°.

**Fluorene — Diphenylene Methane** — $C_{13}H_{10}$ — exists in the fraction of distillation of heavy coal-tar oils, distilling between 300° and 320°. It is also formed by the action of red heat upon diphenyl methane $(C_6H_5)_2CH_2$, and from other diphenyl and phenanthrene derivatives. It crystallizes in colorless leaflets, having a violet fluorescence; f. p. 113°; b. p. 295°; very soluble in ether and in benzene, sparingly soluble in alcohol. Its picric acid compound forms red needles, f. p. 81°.

The constitutional formula of fluorene is given on p. 438. It may be considered as formed by fusion of two benzene rings and one pentacarbocyclic ring, with absorption, consequently, of all but one of the carbon atoms of the latter. Or it may be considered as diphenylene methane, i. e., methane in which 2H are replaced by two phenylene groups, externally united: $\begin{matrix} C_6H_4 \\ | \\ C_6H_4 \end{matrix}\!\!>\!CH_2$. It is, indeed, closely related to other diphenylene compounds, in which the $CH_2$ group is replaced by other bivalents, as by O, S, and NH, in diphenylene oxid, sulfid and imid (carbazole, p. 467). Other fluorene derivatives are also known containing both diphenylene and diphenyl (p. 446) groups, or two diphenylenes, as **diphenylene-diphenylethylene**, $(C_6H_4)_2C{:}C(C_6H_5)_2$, and **bidiphenylene ethane**, $(C_6H_4)_2$-$CH.CH(C_6H_4)_2$.

**Naphthalene**—$C_{10}H_8$ — is obtained commercially from the fraction

of coal-tar distillation passing between 180° and 300°. It crystallises in shining plates; f. p. 79°; b. p. 218°; volatile at all temperatures, giving off a peculiar, tarry odor (white tar, moth-balls); sparingly soluble in cold alcohol, readily soluble in hot alcohol, ether and benzene. It is used in the arts in the preparation of phthalic acid and its derivatives, of the naphthols, etc., and of a great number of naphthalene dyes, for the carburation of water-gas, and against moths. Its picric acid compound fuses at 149°.

Naphthalene is undoubtedly formed in the distillation of coal by condensation of lower hydrocarbons under the influence of heat, a formation which may be imitated by conducting a mixture of benzene vapor with acetylene, or with ethylene, through a tube heated to redness. With ethylene, cinnamene (p. 387) is formed as an intermediate product. Naphthalene derivatives are also formed by condensation of several monobenzenic derivatives with unsaturated lateral chains. Thus α naphthol is produced from phenyl-isocrotonic acid: $C_6H_5\diagup^{CH=CH}_{HOOC.CH_2}=C_6H_4\diagup^{CH=CH}_{C(OH):CH}+H_2O$; and naphthalene itself is formed when phenylbutylene vapor is passed over heated lime: $C_6H_5.CH_2.CH_2.CH:CH_2 = C_6H_5\diagup^{CH=CH}_{CH=CH}+2H_2$. Oxidizing agents convert naphthalene into naphthoquinones (p. 444), and into benzenecarboxylic acids, among others into phthalic acid, $C_6H_4(COOH)_2$. Sulfuric acid forms with it sulfonic acids.

**Naphthalene Homologues** — formed by substitution of alkyls for hydrogen, exist in coal-tar, and are formed by the action of alkyl iodids or bromids upon naphthalene in presence of $Al_2Cl_6$.

**Acenaphthene** — 1, 8 — (or peri-, p. 442) **Ethylene naphthylene**, $C_{10}H_6:\diagup^{CH_{2(1)}}_{CH_{2(8)}}$, is formed when α ethyl-naphthalene is passed through a red-hot tube, and also exists in coal-tar. By oxidation, nitration, etc., it yields a series of peri-naphthalene derivatives.

**Hydronaphthalenes** and their substitution products are derived from naphthalene by rupture of one or more of the double bonds, in the same manner as the hydroaromatic compounds are derived from benzene (pp. 443, 431).

**Anthracene** — $C_{14}H_{10}$ — is obtained commercially from the "green oil" of coal-tar, distilling above 270°; and is used in the manufacture of alizarin dyes (artificial madder). It is formed from benzene and acetylene, or methylene bromid, in presence of $Al_2Cl_6$. It crystallizes in colorless plates, having a fine blue fluorescence; f. p. 213°; b. p. 351°; sparingly soluble in benzene and in carbon disulfid, which are its best solvents. Oxidizing agents convert it into anthraquinone. Its picric acid compound forms red needles, f. p. 138°.

The constitution of anthracene, given on p. 438, is proven by the formation of anthraquinone, which is diphenylene diketone: $C_6H_4:(CO)_2:C_6H_4$, in which the internal bond is liberated.

**Phenanthrene**—$C_{10}H_{14}$—isomeric, with anthracene, accompanies that hydrocarbon in coal-tar. It is also formed by condensation of many benzene compounds when their vapor is passed through a red-hot tube. It crystallizes in colorless plates; f. p. 99°; b. p 340°; sublimes readily at lower temperatures; soluble in benzene, ether and hot alcohol, the solutions having blue fluorescence. Oxidizing agents convert it into phenanthroquinone (p. 444). Its picric acid compound forms yellow needles, f. p. 144°.

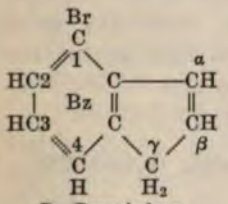
Phenanthrene is closely related to fluorene (p. 439), and to diphenyl (p. 446). It is considered as diphenyl, $HC\langle\begin{smallmatrix}CH:CH\\CH.CH\end{smallmatrix}\rangle C.C\langle\begin{smallmatrix}CH:CH\\CH.CH\end{smallmatrix}\rangle CH$, in which the two ortho positions (o) are united by the group —CH:CH—, while fluorene is diphenyl in which the same positions are united by the group —CH—.

**Chrysene**—$\begin{smallmatrix}C_6H_4-CH\\|\quad\quad\|\\C_{10}H_6-CH\end{smallmatrix}$—f. p. 250°; b. p. 448°—and **Picene**—$\begin{smallmatrix}C_{10}H_6-CH\\|\quad\quad\|\\C_{10}H_6-CH\end{smallmatrix}$—f. p. 364°; resemble phenanthrene in structure, except that they contain one and two double naphthalene rings respectively in place of benzene nuclei. They exist in the coal-tar residues.

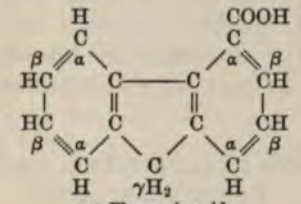
## HALOID DERIVATIVES—ORIENTATION.

The complex character of the nuclei in these hydrocarbons indicates the possible existence of a greater number of isomeres than are met with in the monobenzenic series.

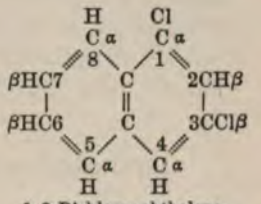
With **indene** different products are obtained by substitution in the benzene ring and in the three pentol positions. The former are designated by the abbreviations Bz, the latter by the Greek letters $\alpha$, $\beta$, $\gamma$. Thus Bz-brom-indene:



Bz-Brom-indene.



α-Fluorenic acid.



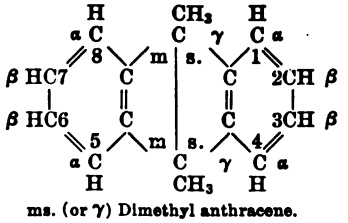
1, 3-Dichlornaphthalene.

Bi-substituted derivatives are o-, m-, and p- in the benzene ring, and $\alpha$, $\beta$, $\gamma$ in the pentol ring. Several chlorindones are known, up to **perchlorindone**: $C_6Cl_4:C_3Cl_2O$.

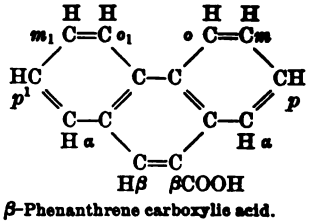
There are three distinct positions of monosubstitution in the fluorene nucleus: (1) the four positions in the benzene rings nearest to the pentol ring, designated as $\alpha$; (2) the four positions furthest removed therefrom, designated as $\beta$, and (3) the single position in the pentol ring, designated as $\gamma$. A dibromid and a tribromid are known.

The naphthalene haloids and other products of substitution have been better studied. There are two positions of monosubstitution, the four $\alpha$ positions nearest to the fusion of the two rings, and the four $\beta$ positions, furthest removed therefrom. Both $\alpha$ and $\beta$ fluorids, chlorids, bromids, and iodids are known. There are ten possible isomeres of each bisubstituted derivative. These are distinguished by using the numerals attached to the several positions as given above, or by the use of prefixes, as follows: 1, 2-ortho, 1, 3-meta, 1, 4-para, 1, 5-ana, 1, 6-epi, 1, 7-kata, 1, 8-peri, 2, 3-allortho, 2, 6-amphi, 2, 7-pros. The ten possible dichlorids are known. In all there are 75 possible naphthalene chlorids, of which 26 are known, and as many bromids, etc.

In anthracene there are three positions of monosubstitution: the four $\alpha$ positions nearest to the uniting groups in the benzene rings; the four $\beta$ positions furthest removed therefrom; and the two $\gamma$, or "meso" (=ms.), positions in the uniting groups (see below). The $\gamma$ mono- and di-chlorin and bromin compounds are formed in preference.



ms. (or $\gamma$) Dimethyl anthracene.



$\beta$-Phenanthrene carboxylic acid.

In phenanthrene there are five positions of monosubstitution: one in each of the o-, $o_1$-, m-, $m_1$-, p-, and $p_1$- positions of the diphenyl (p. 446), the two remaining m-positions of the diphenyl, designated as $\alpha$, and the two positions in the connecting group, –C:C–, designated as $\beta$. Chlorids are known as high as the octochlorid, and bromids as high as the heptabromid.

## PHENOLS, ALCOHOLS, ALDEHYDES, KETONES, QUINONES, CARBOXYLIC ACIDS.

The **phenols**, particularly those of naphthalene, the **oxynaphthalenes**, or **naphthols**, are the most important of those compounds. The naphthols exist in coal-tar, and are also manufactured syntheti-

cally by the methods indicated below. They readily form ethers, and with ammonia they produce the corresponding naphthylamins. Both naphthols are used medicinally as antiseptics.

**α-Naphthol** — $C_{10}H_7.(OH)_\alpha$ — is obtained by heating phenyl-isocrotonic acid (p. 440); also by boiling an aqueous solution of diazonaphthalene nitrate with nitrous acid, or by fusing α-naphthalene-sulfonic acid with KHO.

It crystallizes in colorless prisms; f. p. 95° (203° F.); b. p. 280° (536° F.); nearly insoluble in water, soluble in alcohol and in ether; is easily volatile, and has the odor of phenol. It gives a transient violet color with $Fe_2Cl_6$ and a hypochlorite. With nitrous acid it forms **2, 1 and 4, 1 nitroso-naphthols.** Potassium chlorate and hydrochloric acid oxidize it to dichloro-naphthoquinone. Nascent hydrogen (sodium and alcohol) reduce it to **ar-tetrahydronaphthol** (below). Its acetate fuses at 46° (114.8° F.).

**β-Naphthol**—$C_{10}H_7(OH)\beta$—is prepared industrially by fusion of sodium β-naphthalene-sulfonates with NaHO, for use in the manufacture of a number of dyes, among which are **Campobello yellow** and the **tropeolins.** It crystallizes in colorless, silky plates, which turn dark in daylight; has a faint phenol-like odor, and a sharp, burning taste; f. p. 123° (253.4° F.); b. p. 286° (514.8° F.); sparingly soluble in water, readily soluble in alcohol and in ether. It gives a greenish color with $Fe_2Cl_6$. Its acetate fuses at 70° (158° F.).

**Substituted Naphthols.**—Both naphthols form a great number of derivatives by substitution of other groups for hydrogen atoms. Many of these are important dyes. Thus **Martius yellow** is the Na salt of **2, 4-dinitro-α-naphthol,** a poisonous pigment sometimes used to color butter and confectionery. **Naphthol yellow** is the dipotassium salt of **dinitro-α-naphthol-8-sulfonic acid.** The naphthols combine easily with the diazo- and azo-compounds (p. 426) to form a number of **azo-naphthol** derivatives, several of which are important dyes, as the **naphthol oranges** and **Bieberich scarlet.** A great variety of **naphthol-sulfonic acids** have also been prepared for use in the color industry, as in the preparation of the various **ponceau** and **Bordeaux** dyes. These sulfonic acids, being basic by their OH group and acid by the $HSO_3$ group, form lactone-like compounds (p. 320), which are called **sultones.**

**Tetrahydronaphthols** are formed by the introduction of four H atoms into one of the benzene rings, by the action of nascent hydrogen upon the naphthols. If the hydrogenation occur in the ring containing the OH, one product is obtained, designated by the prefix **ac-**, whereas if it occur in the other ring a different substance is produced, designated by the prefix **ar-**.

**Anthraphenols.** — Three monophenols, $C_{14}H_9(OH)$, are known:

α and β anthrols, which behave like phenols and naphthols; and ms- (or γ) oxyanthracene, or anthranol (p. 442), which is readily oxidized to anthraquinone (below). Two Bz-dioxyanthracenes, $OH.C_6H_3:(CH)_2:C_6H_3.OH$, called chrysazol and rufol, are also known.

Alcohols of this series are known; some primary: as the

Naphthyl Alcohols — $C_{10}H_7.CH_2OH$ — which are formed by the action of nitrous acid upon the corresponding amins (p. 241). The α alcohol fuses at 50°; the β boils at 80°.

Fluorene Alcohol — $\begin{matrix}C_6H_4\\|\\C_6H_4\end{matrix}\!\!>\!CH.OH$ — f. p. 153°, is formed by reduction of fluorene ketone (below).

Naphthyl Aldehydes — $C_{10}H_7.CHO$ — are obtained by oxidation of the alcohols. The α aldehyde boils at 291°; the β fuses at 59°.

The ketones are either ring ketones, such as those of indene and fluorene, or the CO group is in a lateral chain, as in the naphthalene ketones.

γ-Indone — $C_6H_4:\begin{matrix}CH\\CO\end{matrix}\!\!>\!CH$ — is known in its Cl and Br derivatives; also α and β hydrindones, $C_6H_4:\begin{matrix}CH_2\\CO\end{matrix}\!\!>\!CH_2$ and $C_6H_4:\begin{matrix}CH_2\\CH_2\end{matrix}\!\!>\!CO$.

Fluorene Ketone — Diphenylene Ketone — $\begin{matrix}C_6H_4\\|\\C_6H_4\end{matrix}\!\!>\!CO$ — f. p. 84°, is formed by oxidation of fluorene with chromic acid mixture, and also from diphenic acid, $\begin{matrix}C_6H_4.COOH\\|\\C_6H_4.COOH\end{matrix}$.

Naphthyl-methyl Ketone — $C_{10}H_7.CO.CH_3$ — is formed by the action of acetyl chlorid upon naphthalene in presence of $Al_2Cl_6$.

Both aldehydes and ketones form oxims and hydrazones (pp. 360, 429).

Quinones. — Naphthalene, anthracene and phenanthrene readily yield quinones (p. 396), some of which are technically prepared by oxidizing the hydrocarbons in acetic acid solution by chromic acid; or from the dioxy- or diamido-compounds.

Naphthoquinones. — Oxidation of naphthalene produces α naphthoquinone, $C_{10}H_6:O_{2(1,4)}$, which crystallizes in yellow needles, fusible at 125°. The α-β quinone, $C_{10}H_6:O_{2(1,2)}$, is formed by oxidation of β amido-α-naphthol, and crystallizes in red needles, fusible at 115°. Both naphthoquinones form oxims and hydrazones, some of which are used in the color industry.

Anthraquinone — Diphenylene Diketone — $C_6H_4:(CO)_2:C_6H_4$ — is commercially manufactured by oxidation of anthracene. It forms yellow needles; f. p. 285°; b. p. 382°. It forms an oxim with hydroxylamin, and sulfonic acids with $H_2SO_4$, as well as chlorin, bromin and oxy- derivatives.

**Alizarin**—**1, 2-Dioxyanthraquinone**—$C_6H_4:(CO)_2:C_6H_2:(OH)_2$—is prepared industrially by the action of fused NaHO upon anthraquinone-monosulfonic acid, and is also formed by fusion of several other anthraquinone derivatives with caustic alkalies. It is the coloring principle of madder (*Rubia tinctoria*), and the artificial product has now completely displaced madder in dyeing.

**Purpurin**—**1, 2, 4-Trioxyanthraquinone**—$C_6H_4:(CO)_2:C_6H:(OH)_3$—is another constituent of madder, also obtained artificially by oxidation of alizarin, or from tribromo-anthraquinone.

Both alizarin and purpurin form nitro- and amido- substitution products which are also used as dyes; alizarin orange, blue and brown.

Several **oxymethylanthraquinones** are active principles of purgative drugs. **Chrysophanic, or rhëic acid,** which exists in senna, rhubarb, cascara, goa-powder, is **dioxymethylanthraquinone**, $C_6H_4:(CO)_2:C_6H.CH_3:(OH)_2$. Reducing agents convert it, first into **chyrsarobin**, $C_{30}H_{36}O_7$ (?), which also exists in goa-powder, and finally into methylanthraquinone. **Emodin**, which exist in *Rhamnus frangula* (p. 412) and in rhubarb, is **trioxymethylanthraquinone**, $C_6H_4:(CO)_2:C_6.CH_3:(OH)_3$.

**Carboxylic Acids.**—A great variety of acids are derivable from indene, hydrindene, fluorene, anthracene and phenanthrene by substitution of COOH groups for hydrogen.

**Naphthalene Monocarboxylic Acids—Naphthoic Acids**—$C_{10}H_7.COOH$—are formed by hydrolysis of their nitrils. The α acid fuses at 160°; the β at 182°. Their homologues are **naphthyl-fatty acids.** They form a great variety of substitution products, nitro-, amido-, etc., among which are the **naphthol-carboxylic acids**, $C_{10}H_6.OH.COOH$, which readily decompose into water and lactones (p. 320). The **naphthalene di- and poly-carboxylic acids** are very numerous (p. 442), the best known being **naphthalic, or 1, 8-naphthalene dicarboxylic acid,** formed by the oxidation of acenaphthene, $C_{10}H_6:(CH_2)_{2(1,8)}$.

## NITROGEN DERIVATIVES.

Naphthalene, anthracene, and phenanthrene form a number of nitro, amido, azo, and hydrazin derivatives, of which only a few of the naphthalic compounds require brief mention.

**Naphthylamins—Amidonaphthalenes**—$C_{10}H_7.NH_2$. Both α and β compounds are formed by reduction of the corresponding nitronaphthalenes, $C_{10}H_7.NO_2$; or by the action of ammonia upon the naphthols in presence of zinc chlorid: $C_{10}H_7.OH+NH_3=C_{10}H_7.NH_2+H_2O$, the latter a method of formation which is not realized with the amidobenzenes (p. 419). The α amin crystallizes in flat needles;

f. p. 50° (122° F.); b. p. 300° (572° F.); insoluble in water, soluble in alcohol and ether; becomes red on exposure to air; has a persistent and disagreeable odor. On moderate oxidation it forms a blue compound, oxynaphthylamin, $C_{10}H_6\langle^{NH_2}_{OH}$; on more complete oxidation α naphthoquinone. The β amin crystallizes in plates; f. p. 112° (233.6° F.); b. p. 294° (561.2° F.); dissolves in hot water, forming a blue-fluorescent solution. On oxidation it forms phthalic acid. Tetrahydro β-naphthylamin, $C_{10}H_{11}.NH_2$, is a very active mydriatic.

Several naphthylamin-sulfonic acids are manufactured in the color industry, as well as diazo- and azonaphthalene compounds.

## D. DIPHENYL AND ITS DERIVATIVES.

Diphenyl, $C_6H_5.C_6H_5$, is the type of the hydrocarbons, known as phenylbenzenes, formed by the substitution of phenyl, toluyl, benzyl, etc., for atoms of hydrogen in benzene (see formula of $p_2$-diamidodiphenyl, p. 384). Thus we have, besides diphenyl, toluyl-benzene, $C_6H_5.C_6H_4.CH_3$, diphenyl-benzene, $C_6H_4:(C_6H_5)_2$, and triphenylbenzene, $C_6H_3:(C_6H_5)_3$. These hydrocarbons are the parent substances of a great number of substitution products. The monosubstituted compounds are o-, m-, or p-, with reference to the point of union of the benzene rings. In the bi- and polysubstituted derivatives the substituents may be introduced into the same or into different rings. Bi-substitution of bivalent groups for $H_2$ in the $o$-$o_2$-positions produces compounds belonging to other series of our classification. Thus fluorene and phenanthrene (p. 441) are derivable from diphenyl by substitution of $-CH_2-$ and of $-CH.CH-$ respectively in the $o$-$o_2$- positions. Diphenylene oxid and sulfid and carbazole (p. 467) are similarly derivable from diphenyl by substitution of O, S, and NH.

Diphenyl—Phenylbenzene—$C_6H_5.C_6H_5$—exists in small quantity in gas-tar. It is formed by the action of sodium upon monobromobenzene: $2C_6H_5Br+Na_2=C_6H_5.C_6H_5+2NaBr$; or by passing benzene vapor through a red-hot tube; or by the interaction of diazobenzene chlorid and benzene in presence of aluminium chlorid: $C_6H_5.N:NCl+C_6H_6=C_6H_5.C_6H_5+HCl+N_2$. It crystallizes in large plates; f. p. 70° (158° F.); b. p. 254° (489.2° F.); soluble in glacial acetic acid and in amylic alcohol. Nascent hydrogen converts it into tetrahydro-diphenyl, $C_{12}H_{14}$. With methylene chlorid, in presence of $Al_2Cl_6$ it forms fluorene: $C_6H_5.C_6H_5+CH_2Cl_2=C_6H_4.CH_2.C_6H_4+2HCl$. Difluor-diphenyl, $C_6H_4F.C_6H_4F$, is a white, crystalline powder, used as an antispasmodic under the name antitussin.

**Amido-diphenyls, toluyls,** etc., can be obtained by reduction of the corresponding nitro-compounds. One of these, **benzidin,** or **$p_2$-diamido-diphenyl** (formula p. 384), is a product of technical importance, which is, however, manufactured by reduction of azobenzene in acid solution. Azobenzene, $C_6H_5.N:N.C_6H_5$, first forms hydrazobenzene, $C_6H_5.NH.NH.C_6H_5$ (p. 428), which by further hydrogenation and transposition, yields benzidin, $NH_{2(4)}.C_6H_4.C_6H_4.NH_{2(4)}$. Benzidin serves for the manufacture of a number of azo dyes, which are sulfonic or carboxylic acids, or their salts. Among these benzidin dyes are Congo-yellow and Congo-red.

**Oxydiphenyls** are the phenols of these hydrocarbons, and are formed by fusing the benzenic phenols with KHO. The hexaoxydiphenyl derived from pyrogallol (p. 395) yields a quinone (p. 396) whose methylic ester is **cœrulignone,** $O_2:C_{12}H_6(OCH_3)_4$, the amido derivatives of which form a number of blue, violet and black dyes.

## E. DIPHENYL-PARAFFINS, DIPHENYL-OLEFINS, DIPHENYL-ACETYLENES.

The hydrocarbons of this series may be considered as derived from the aliphatic hydrocarbons by substitution of two (or more) phenyl groups for hydrogen :

$C_6H_5.CH_3$—Phenyl-methane=Toluene=Methyl-benzene (p. 386).
$C_6H_5.CH_2.C_6H_5$—Diphenyl-methane=Benzyl-benzene (formula p. 384).
$(C_6H_5)_2:CH.C_6H_5$—Triphenyl-methane.
$(C_6H_5)_2:Si:(C_6H_5)_2$—Tetraphenyl-silicon (C compound unknown).
$C_6H_5.CH_2.CH_2.C_6H_5$—Sym. Diphenyl-ethane=Dibenzyl.
$(C_6H_5)_2:CH.CH_3$—Unsym. Diphenyl-ethane.
$C_6H_5.CH:CH.C_6H_5$—Sym. Diphenyl-ethylene=Stilbene.
$C_6H_5.C\equiv C.C_6H_5$—Diphenyl-acetylene=Tolane.

**Diphenyl-methane—Benzyl-benzene**—is produced by the action of benzyl chlorid upon benzene in presence of aluminium chlorid: $C_6H_5.CH_2.Cl+C_6H_6=C_6H_5.CH_2.C_6H_5+HCl$. It is a crystalline solid; f. p. 27° (80.6° F.); b. p. 262° (503.6° F.); soluble in alcohol, ether, and chloroform; has an odor resembling that of the orange.

**Triphenyl-methane**—is formed by the action of chloroform upon benzene in presence of aluminium chlorid: $3C_6H_6+CHCl_3=(C_6H_5)_2:CH.C_6H_5+3HCl$. It is a crystalline solid; f. p. 92° (197.6° F.); b. p. 360° (680° F.); soluble in ether and in chloroform. It is converted into a trinitro-derivative by fuming $HNO_3$; and this, in turn, is converted by nascent H into **leuco-pararosanilin,** $CH.(C_6H_4.NH_2)_3$.

**Stilbene—Toluylene—Sym. Diphenyl-ethylene**—is formed by distillation of benzyl sulfid; by reduction of benzoic aldehyde; or by

distillation of the phenylic esters of fumaric (p. 375) or cinnamic (p. 402) acids. It forms large, glistening prisms or plates; f. p. 124° (255.2° F.); b. p. 306° (582.8° F.). It forms a number of haloid and other derivatives.

Tolane—Diphenyl-acetylene—is formed by the action of KHO upon stilbene bromid. It is a crystalline solid; f. p. 60° (140° F.).

Diphenyl-diacetylene — $C_6H_5.C{\equiv}C.C{\equiv}C.C_6H_5$ — is formed by moderate oxidation of copper phenyl-acetylid, $C_6H_5.C{\equiv}C.Cu.C{\equiv}C.C_6H_5$, as a crystalline solid; f. p. 88° (190.4° F.). Its o, o₂-dinitro-derivative is converted into indigo-blue (p. 466) by reduction.

## PHENOLS, ALCOHOLS, KETONES, AND CARBOXYLIC DERIVATIVES.

Phenolic derivatives of these hydrocarbons are known, which contain hydroxyls in one or more of the phenyl groups.

Diphenyl Carbinol—Benzhydrol—$C_6H_5.CHOH.C_6H_5$—is the simplest alcohol of this series. It is formed in colorless crystals; f. p. 68°; b. p. 298°; by reduction of benzophenone with sodium amalgam, $C_6H_5.CO.C_6H_5 + H_2 = C_6H_5.CHOH.C_6H_5$. Its tetramethyl-diamido- derivative, $CHOH\langle^{C_6H_4.N(CH_3)_2}_{C_6H_4.N(CH_3)_2}$, forms colorless crystals, which dissolve in acetic acid with an intense blue color. It is formed by the action of lead peroxid and acetic acid upon tetramethyl-diamido-diphenyl methane, which is produced by heating dimethyl anilin with formaldehyde and a little sulfuric acid: $2C_6H_5.N(CH_3)_2 + H.CHO = CH_2\langle^{C_6H_4.N(CH_3)_2}_{C_6H_4.N(CH_3)_2} + H_2O$. These reactions are used as a test for formaldehyde.

Triphenyl Carbinol, $(C_6H_5)_3C.OH$, and diphenyl-m-toluyl carbinol, $(C_6H_5)_2:C(OH).C_6H_4.CH_{3(3)}$, are alcohols, whose triamido-derivatives are pararosanilin and rosanilin. They are formed by oxidation of the hydrocarbons. They form nitro- and amido-derivatives of technical importance.

The benzophenones, the ketones of this series, correspond to the phenones (p. 400), from which they differ in containing two phenyls in place of one; and they bear the same relation to the benzoic acids that the acetones (p. 261) do to the fatty acids. They are produced by oxidation of the hydrocarbons; by the action of $P_2O_5$ upon a mixture of a benzene hydrocarbon and a benzoic acid; or by the action of phosgene or of an acidyl chlorid upon benzene in presence of aluminium chlorid.

Benzophenone — Diphenyl-ketone—$C_6H_5.CO.C_6H_5$—forms large rhombic prisms; f. p. 48° (118.4° F.); b. p. 305° (581° F.); soluble in alcohol and ether. Sodium amalgam reduces it to benzhydrol,

or **diphenyl carbinol**, $(C_6H_5)_2:CH.OH$. Benzophenone is the parent substance of a great number of substitution products, some of which are used in the color industry.

**Benzoin**—$C_6H_5.CH(OH).CO.C_6H_5$—which exists in crude oil of bitter almonds, is a keto-alcohol corresponding to **hydrobenzoin**, or **toluylene glycol**, $C_6H_5.CH(OH).CH(OH).C_5H_5$, which is formed by the action of nascent H upon benzoic aldehyde (p. 398).

**Benzil—Dibenzoyl**—$C_6H_5.CO.CO.C_6H_5$—is a diketone, obtained by the action of moist silver oxid upon stilbene bromid.

**Carboxylic acids** derived from the diphenyl-methanes, such as **benzoyl-benzoic acids**, $C_6H_5.CO.C_6H_4.COOH$, and acids derived from stilbene and from diphenyl-diacetylene are known. But few of the carboxylic acids derivable from triphenylmethanes are known, owing to their tendency to lose water and form lactones. Among these lactones are the phthaleïns and numerous other dyes, such as rosolic acid and the aurines.

The **phthalids** of this class may be considered as derived from phthalid (p. 407), $C_6H_4\langle^{CO_{(1)}}_{CH_{2(2)}}\rangle O$, which is the lactone of o-oxymethylbenzoic acid, $C_6H_4\langle^{COOH_{(1)}}_{CH_2OH_{(2)}}$, by substitution of phenyl for hydrogen in the $CH_2$ group. Thus **diphenyl phthalid**, obtained by oxidation of triphenyl methane o-carboxylic acid, $C_6H_4\langle^{COOH_{(1)}}_{CH(C_6H_5)_{2(2)}}$, has the constitution: $C_6H_4\langle^{CO_{(1)}}_{C_{(2)}=(C_6H_5)_2}\rangle O$. The phthaleïns have been considered as oxyphenyl ketonic derivatives of phthalic acid, as indicated on p. 396, or as lactones derivable from phthalid by substitution of oxyphenyl groups. Thus phenol phthaleïn, $C_6H_4\langle^{CO_{(1)}}_{C_{(2)}=(C_6H_4.OH)_2}\rangle O$.

## NITROGEN-CONTAINING DERIVATIVES.

Among the great number of nitro- and amido-derivatives of these hydrocarbons the most important are the amido-derivatives of triphenyl-carbinol (p. 448). From those in which two or three of the amido groups occupy the para positions with regard to the C(OH) group, or from their alkyl derivatives, a number of important dyes, red, green, violet, blue, and brown, are manufactured.

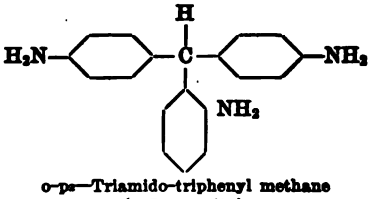
**p-Amido-triphenylmethane**—$(C_6H_5)_2:CH.C_6H_4.NH_{2(4)}$—is formed by the action of benzhydrol upon anilin chlorid in presence of zinc chlorid. The corresponding carbinol forms salts which have no coloring power.

**$p_2$-Diamido-triphenylmethane**—$C_6H_5.CH:(C_6H_4.NH_{2(4)})_2$—is produced by the interaction of anilin chlorid and benzoic aldehyde in

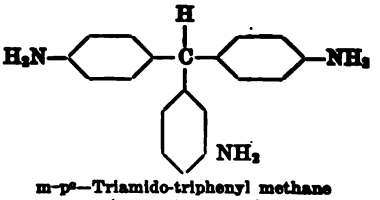
presence of zinc chlorid, and by other methods. The base is a yellow, imperfectly crystalline solid, insoluble in water, soluble in alcohol and in benzene; which forms blue salts. The corresponding carbinol, $C_6H_5.C(OH):(C_6H_4.NH_{2(4)})_2$ forms a chlorid which is a reddish-violet dye.

$p_2$-Tetramethyl-diamido-triphenylmethane — $C_6H_5.CH:[C_6H_4.N(CH_3)_{2(4)}]_2$—is manufactured by the action of sulfuric or hydrochloric acid upon benzoic aldehyde and dimethyl-anilin. It and its carbinol are almost colorless bases, which form salts which are brilliant green dyes, leucomalachite green and malachite green, or bitter almond-oil green.

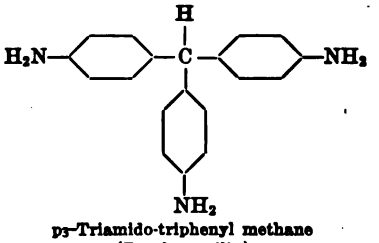
Triamido-triphenyl methanes and their alkyl derivatives (see below) are known as leucanilins (λευκός=white) from the fact that, while some of their derivatives are brilliantly colored, they are colorless, or nearly so. By oxidation they yield carbinols, formed by the substitution of OH for H in the connecting group CH, known as rosanilins, which are powerful triacid bases, whose salts are the dyes referred to. The most important industrially are those having at least two amido-groups in para positions. Their constitution is indicated by the following formulae:



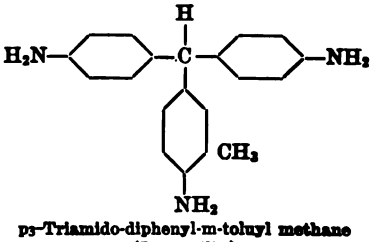
o-$p_2$—Triamido-triphenyl methane (o-Leucanilin).



m-$p_2$—Triamido-triphenyl methane (Pseudoleucanilin).



$p_3$-Triamido-triphenyl methane (Paraleucanilin).



$p_3$-Triamido-diphenyl-m-toluyl methane (Leucanilin).

or, by a different form of expression for the corresponding carbinols; the rosanilins:

$$HO.C\begin{cases}C_6H_4.NH_{2(4)}\\C_6H_4.NH_{2(4)}\\C_6H_4.NH_{2(o)}\end{cases}$$

$$HO\,C\begin{cases}C_6H_4.NH_{2(4)}\\C_6H_4.NH_{2(4)}\\C_6H_4.NH_{2(3)}\end{cases}$$

$$HO.C\begin{cases}C_6H_4.NH_{2(4)}\\C_6H_4.NH_{2\,4)}\\C_6H_4.NH_{2(4)}\end{cases}$$

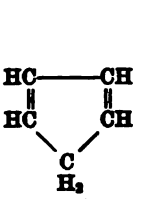
$$HO.C\begin{cases}C_6H_4.NH_{2(4)}\\C_6H_4.NH_{2(4)}\\C_6H_3.CH_{3(3)}.NH_{2(4)}\end{cases}$$

Of these the $p_3$-triphenyl, and the $p_3$-diphenyl-m-toluyl carbinols and their methyl, ethyl, benzyl, and phenyl derivatives are extensively used in the color industry. **Fuchsine, anilin red,** or **magenta** consists chiefly of the acetate or hydrochlorid of $p_3$-triamido-diphenyl-m-toluyl carbinol, or rosanilin. It is manufactured by oxidation of "anilin oil" (p. 420), which is a mixture of anilin, and o- and p-toluidin, by heating with a mixture of nitro-benzene, hydrochloric acid, and iron filings. Formerly arsenic acid was used as an oxidant, when the fuchsin was obtained as a poisonous arsenite. Fuchsin forms green crystals, having a metallic luster, soluble in water and in alcohol, to which it communicates a bright-red color. This color is discharged by sulfurous acid, and regenerated by aldehydes, and such a decolorized magenta solution is used as a reagent for the detection of aldehydes (Schiff's reagent).

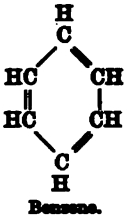
By the action of methyl iodid upon fuchsin a number of methylated derivatives are obtained, which are violet dyes, such as **crystal violet, Hofmann's violet, dahlia,** etc. By further methylation of the violets, green dyes are formed, as the **iodin greens,** and **aldehyde green.** By substitution of phenyl in place of methyl, a number of blue dyes, as **Lyons blue, soluble blue** and **alkali blue** are obtained. **Pyoktanin-blue, dahlia,** is penta- and hexa-methyl pararosanilin hydrochlorid, produced from dimethyl anilin. It is a violet powder, soluble in water and very diffusible, non-poisonous and used internally as an antiseptic. **Pyoktanin-yellow,** used medicinally for the same purposes as the blue, is the hydrochlorid of imido-tetramethyl-diamido-diphenyl methane, $HN:C\langle^{C_6H_4.N:(CH_3)_2}_{C_6H_4.N:(CH_3)_2}$. **Triphenyl-pararosanilin,** $HO.C:(C_6H_4.NH.C_6H_5)_3$, is the base of a number of blue dyes, among which is **methyl-blue,** the sodium salt of its trisulfonic acid, which has been used locally in diphtheria. It is poisonous, and has caused death by its administration in mistake for methylene-blue (p. 459).

## HETEROCYCLIC COMPOUNDS.

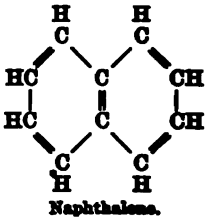
**These compounds differ from the carbocyclic in that they contain elements other than carbon as constituents of the nuclei. They form series parallel to the carbocyclic, from which, indeed, they may be considered as being derived by substitution in the rings. Thus thiophene corresponds to pentole, pyridin to benzene, and quinolin to naphthalene:**



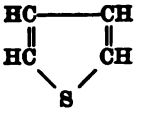
Pentole.



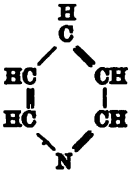
Benzene.



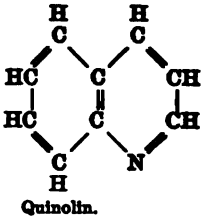
Naphthalene.



Thiophene.



Pyridin.



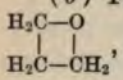
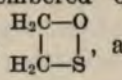
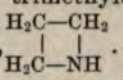
Quinolin.

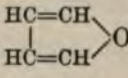
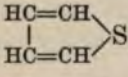
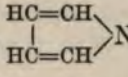
The elements which can be thus introduced into a cyclic nucleus are few; oxygen, sulfur, selenium, phosphorus and nitrogen being the only ones now known to enter into such formation, and of these the nitrogen-containing compounds are far the most numerous and the most important. The facility with which the N atom takes the place of the methine group,—CH=, in the benzene ring is to be anticipated from their equivalence. Pyridin also resembles benzene in its general characters, and, on the other hand, the five membered compounds, furfurane, thiophene and pyrrole, have general characters similar to those of benzene, from which they may be considered as being derived by substitution of the bivalents O, S, and NH for one of the three acetylenes,—CH:CH—, of benzene. The number of hetero-atoms which may be contained in the nucleus is not limited to one, and five and six membered rings containing as many as four nitrogen atoms, the tetrazoles and tetrazins, are known.

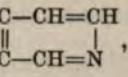
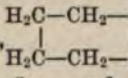
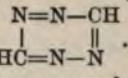
A classification of the heterocyclic compounds requires many subdivisions, because of the great number and variety of these substances, due to the presence of one or more atoms of one or more

of the elements above mentioned, in three, four, five or six membered rings, contained in mono-, di-, tri-, or tetra-nucleate molecules, in which, also, differences in the ring-valence are caused by differences in internal linkage. A broad classification may, however, be here followed, somewhat similar to that for the aromatic substances (p. 384).

A. Mono-nucleate compounds: containing a single nucleus. These may be subdivided into: (*a*) Substances containing three-membered rings; such as ethylene oxid, , sulfid, , and imid, .

(*b*) Four-membered compounds, such as trimethylene oxid,  , thetin,  , and trimethylene imid,  .

(*c*) Five-membered substances, such as furfurane,  , thiophene,  , and pyrrole,  .

(*d*) Six-membered compounds, such as pyridin,  , piperidin,  , and sym. tetrazin,  .

The five- and six-membered compounds are much more numerous and important than the three- and four-membered.

B. Condensed compounds, containing two or more rings, usually five- or six-membered, of which at least one is heterocyclic, fused together, and having two carbon atoms in common. These compounds, which correspond to the condensed benzenic compounds (p. 438), include the indole, quinolin, anthraquinolin, quinoquinolin, and diphenylene derivatives.

C. Compounds containing two (or more) nuclei, one at least heterocyclic, united directly without fusion, corresponding to the diphenyls, and including phenyl-pyridyl, dipyridyl, pyridyl-pyrrole, and pyridyl-piperidyl derivatives.

D. Compounds containing two (or more) nuclei, one at least heterocyclic, united by aliphatic groups, corresponding to the diphenyl-paraffins, and including the "ester-alkaloids" such as atropin, cocain, etc.

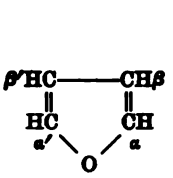
In a more detailed classification the members of the several classes are subdivided into the groups of **mono-, di-, tri-,** and **tetrahetero-atomic compounds,** according as they contain one, two, three or four atoms other than carbon, of like or different kinds, in the ring.

## A.—MONONUCLEATE HETEROCYCLIC COMPOUNDS.

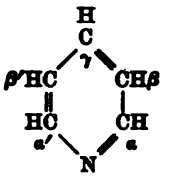
### FIVE MEMBERED RINGS.

The parent substances of these compounds are furfurane, thiophene, and pyrrole* (see p. 453).

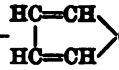
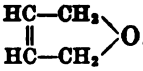
The heterocyclic rings differ from the carbocyclic in that the several carbon atoms are not equal in value, and therefore two different monosubstituted derivatives exist for the five membered rings containing a single hetero-atom, such as furfurane, and three such compounds in six membered rings, such as pyridin, according to the position of substitution with reference to the hetero-atom. These positions are distinguished by the first three letters of the Greek alphabet, as shown in the margin, or, sometimes by numbers. The positions α and α′, and β and β′ are of equal value.

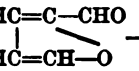


Furfurane.



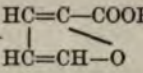
Pyridin.

Furfurane—  —exists in the product of distillation of pine and fir wood, and is also formed by distillation of barium pyromucate (below), and from dihydrofurfurane,  , a product of reduction of erythrol (p. 254). It is a liquid; b. p. 32° (89.6° F.); having a peculiar odor. Its vapor colors a pine shaving moistened with HCl green (pp. 390, 455).

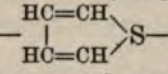
α-Furfuraldehyde—Furfurole—Furole—  —is produced by the dry distillation of sugar or of wood; by the distillation of these substances, or of bran, carbohydrates or glucosids with dilute $H_2SO_4$; by the action of the concentrated acid upon sugar; and by distilling pentoses (p. 265), or glucuronic acid (p. 299) with HCl. It is a colorless liquid; agreeable in odor; b. p. 162° (323.6° F.); soluble in water and in alcohol. Being an aldehyde, it undergoes the reactions common to those substances. In concentrated solution, with urea and a trace of acid, it is colored yellow, changing to blue, to violet and to purple, and finally fading, with formation of a black precipitate (Schiff's reaction). It produces a red color with anilin, a very sensitive reaction for its presence. Paper moistened with anilin

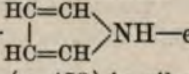
*The usual spelling is pyrrol, furfurol, indol. The terminal e is used because these substances are neither alcohols nor phenols, for whose names the termination ol is reserved.

acetate solution is used. Adamkiewicz' and Liebermann's reactions for the proteins, and Pettenkofer's reaction for the biliary salts, etc., depend upon the formation of furfurole.

**α-Furfurane Carboxylic Acid—Pyromucic acid**—  —

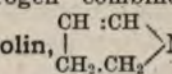
the acid corresponding to furfurole, is produced from that substance by oxidation, also by distillation of mucic and isosaccharic acids (p. 297). It is a solid; f. p. 134° (273.2° F.).

**Thiophene**—  —and its superior homologues, methyl-thiophenes, etc., occur in gas-tar, and accompany the various products, benzene, etc., obtained from it. It is a colorless liquid; b. p. 84° (111.2° F.); which is so nearly that of benzene, 80.5°, that the two substances cannot be separated by distillation. With sulfuric acid and isatin it gives a fine blue color, due to formation of indophenin. Sulfuric acid alone is colored brown by thiophene, which it absorbs; and thiophene may be recovered from the solution by neutralization and distillation.

**Pyrrole**—  —exists in coal-tar and accompanies the pyridin bases (p. 459) in oil of Dippel. It is formed in a great variety of reactions, as by the action of baryta at 150° (303° F.) upon albumens, by the dry distillation of gelatin or of ammonium saccharate, etc. It is a colorless, oily liquid, having the odor of chloroform; b. p. 131° (267.8° F.). Being a secondary amin, it has basic properties, and its imid hydrogen is readily replaced by other atoms or groups. A pine shaving moistened with HCl is colored flame-red by pyrrole (the pine-shaving reaction; see also, Phenol, p. 390). It also yields an indigo-blue color with $H_2SO_4$ and isatin. Heated with dilute acids it gives off ammonia, and a red powder (pyrrole red) is deposited.

The homologous pyrroles, methyl-pyrroles, etc., have reactions similar to those of pyrrole.

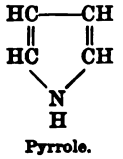
Pyrrole and its homologues form series of substitution products: haloid, nitro-, azo-, carboxylic, etc. Among these is **tetriodopyrrole**, or **iodol**, $C_4I_4NH$, formed as a brown powder by acting upon pyrrole with an ethereal solution of iodin, and used in surgery as a substitute for iodoform, over which it has the advantage of being odorless.

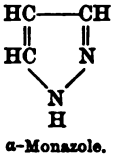
**Hydropyrrole Derivatives**—Nascent hydrogen combines with pyrrole to form, first **dihydropyrrole**, or **pyrrolin**,  , an alkaline liquid, soluble in water; b. p. 91°; and, finally, **tetrahydro-**

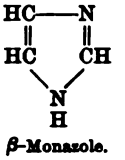
pyrrole, or pyrrolidin, or tetramethylene-imin, $\begin{matrix}CH_2.CH_2\\|\\CH_2.CH_2\end{matrix}\!\!>\!NH$, which bears the same relation to pyrrole that piperidin does to pyridin (p. 461). Pyrrolidin resembles piperidin in its reactions, and also forms an addition product with methyl iodid. It is formed by heating tetramethylene-diamin hydrochlorid (p. 383): $H_2N.(CH_2)_4.NH_2.HCl = NH_4Cl + (CH_2)_4{:}NH$, and constitutes the nucleus of the hygrins (p. 472) and one of those of nicotin (p. 474). It is a strongly alkaline liquid; b. p. 87°. Among the derivatives of pyrrolidin is pyrrolidone, or butyrolactam, $\begin{matrix}CH_2.CH\\|\\CH_2.CO\end{matrix}\!\!>\!NH$, a simple cyclic imid derived from γ-amidobutyric acid (p. 362).

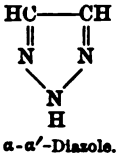
### AZOLES AND THEIR DERIVATIVES.

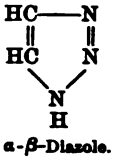
The azoles are derivable from furfurane, thiophene and pyrrole by substitution of one or more nitrogen atoms for methine groups. They are distinguished, according to their parent substances, and the number of nitrogen atoms introduced, as furo-monazoles, thio-diazoles, pyrro-triazoles, etc. There are nine of each of these classes of substances known either as the parent substance or in some of its derivatives. They are distinguished by the lettering indicating the position or positions of the non-imid nitrogen. Thus we have the following pyrazoles:

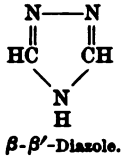

Pyrrole.

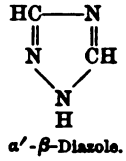

α-Monazole.

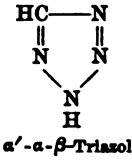

β-Monazole.

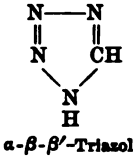

α-α′-Diazole.

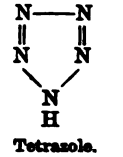

α-β-Diazole.


β-β′-Diazole.


α′-β-Diazole.


α′-α-β-Triazole.

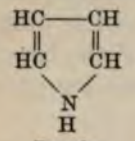

α-β-β′-Triazole.

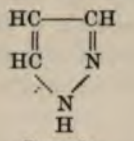

Tetrazole.

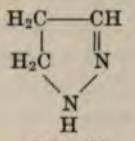
Corresponding to each of these are derivatives, formed by substitution and by modification of the internal linkages. Those derived from pyrro-α-monazole are the most important, and may serve as types. The n-phenyl derivatives (those in which $C_6H_5$ is substituted for H in NH) are the best known, and the most readily obtainable. Pyrro-α-monazole, or pyrazole, is reduced by sodium to dihydropyr-

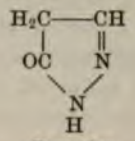
**azole**, or **pyrazolin** (formula below); The phenyl derivative of a **tetrahydropyrazole, phenyl-pyrazolidin,** is also known.

The **pyrazolons** are ketonic derivatives of the pyrazolins, in which O takes the place of $H_2$ in the $\alpha$-position. Thus:

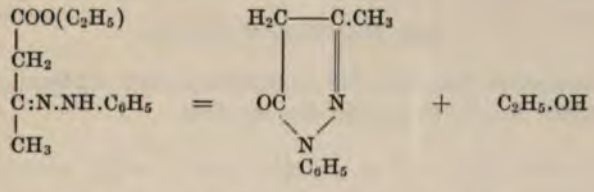

Pyrrole.


Pyrazole.

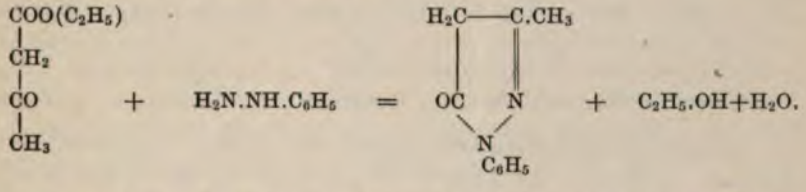

Pyrazolin.


Pyrazolon.

The pyrazolons are obtained from the hydrazones (p. 429) of the esters of the $\beta$ ketone acids (p. 298) by elimination of alcohol, or by the action of phenylhydrazin upon these esters themselves. Thus **1, 3-phenylmethyl-pyrazolon** is formed either from phenylhydrazone-acetoacetic ester:



or from aceto-acetic ester and phenylhydrazin:



**Antipyrin — 1, 2, 3** (or **n-$\alpha$-$\beta$**) — **Phenyldimethyl Pyrazolon** — $C_6H_5N.CO.CH$ / $CH_3N$—$C.CH_3$ — is formed, as its hydroiodid, by heating 1, 3-phenyl-methyl pyrazolon, formed by the second reaction given above, with methyl iodid and methylic alcohol to 100° (212° F.) in sealed vessels. It forms colorless, odorless scales, somewhat bitter in taste; f. p. 110.5° (230.9° F.). A mixture of equal parts of antipyrin and antifebrin (f. p. 112.5°) fuses at 45° (113° F.). Antipyrin is readily soluble in water, alcohol and chloroform, less soluble in ether. With nitrous acid or the nitrites (sp. æth. nitr.), in the presence of free acid, it forms a green, crystalline, sparingly soluble nitro-derivative, which is poisonous. Its solution is colored deep red-brown by $Fe_2Cl_6$, the color being discharged by $H_2SO_4$. Nitrous acid colors its solutions

pyrrole, or pyrrolidin, or tetramethylene-imin, $CH_2$ ... ion of a drop ... then to blood- ... ion of a drop of ... of antipyrin causes ... rin is strongly basic, ... Salipyrin is antipyrin ... acid and the base upon ... hite, crystalline powder, ... line liquid; b. p. 87°. Among the de-

bears the same relation to pyrrole that piper- (p. 461). Pyrrolidin resembles piperidin i- forms an addition product with methyl iodi- tetramethylene-diamin hydrochlorid (p. 33- $NH_4Cl+(CH_2)_4:NH$, and constitutes ... (p. 472) and one of those of nicotin (-

done, or butyrolactam, $\begin{matrix}CH_2.CH\\ |\\ CH_2.CO\end{matrix}>NH$ ... pyrazolon — is obtained in ... p-toluyl-hydrazin in place of ... $C_6H_4.CH_3$ in place of phenyl. ... (276.8° F.); and has a physio- ... antipyrin. Its salicylate is preferred

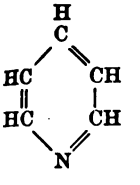
γ-amidobutyric acid (p. 362).

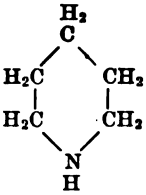
## AZOLES

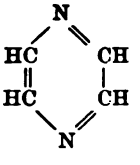
The azoles are deriv- ... by substitution of one ... They are distinguish- ... number of nitrogen ... pyrro-triazoles, et- ... stances known ... derivatives. T- ... position or p- ... following py-

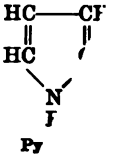
SIX MEMBERED RINGS.

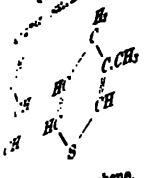
... compounds are known, containing ... in the nucleus:


Pyridin.


Piperidin.


Pyrazin.


Py


δ-Methylthiophene.

The oxygen and sulfur compounds are neither numerous nor important. Some of the former are products of condensation of aliphatic compounds, δ-lactones and δ-anhydrids (p. 320).

*Pyrone (γ)*—*Pyrocomane*—$O\begin{matrix}CH=CH\\ CH=CH\end{matrix}>CO$—is an oxidized derivative of γ furane, produced from comenic acid by the action of heat and constituting the nucleus of comenic, chelidonic, and meconic acids.

*Comenic acid*—$C_5H_3O_2(COOH)$—is produced by the action of hot $H_2O$, of dilute acids, or of bromin water upon meconic acid. It crystallizes in yellowish prisms, rather soluble in $H_2O$. It is monobasic. It is decomposed by heat into $CO_2$ and pyrone.

*Chelidonic acid*—$C_5H_2O_2(OH)COOH$—exists in chelidonium, in combination with the alkaloids sanguinarin and chelidonin. It is a crystalline solid, and a dibasic acid. Heat converts it into comenic acid, which in turn yields pyrone.

**Meconic acid**—$C_5HO_2(OH)(COOH)_2$—is peculiar to opium, in which it exists in combination with a part, at least, of the alkaloids. It crystallizes in small prismatic needles; acid and astringent in taste; loses its Aq at 120° (248° F.); quite soluble in water, soluble in alcohol, sparingly soluble in ether.

With ferric chlorid it forms a blood-red color, which is not discharged by dilute acids or by mercuric chlorid; but is discharged by stannous chlorid and by the alkaline hypochlorites.

Among the six-membered heterocyclic derivatives containing both N and O, or N and S in the nucleus are a number of important dyes: **rosorufin, naphthol blue, Nile blue, Lauth's violet, toluylene red, safranins, indulines,** and

**Methylene blue**—$(CH_3)_2:N.C_6H_3.NS.C_6H_3:N:(CH_3)_2Cl$—which is formed by oxidation of dimethyl-p-phenylene diamin in $H_2S$ solution. A blue powder, sparingly soluble in water. It is used as a dye, as a bacterial stain, and is administered as a antipyretic and antiperiodic.

### SIX-MEMBERED, NITROGEN-CONTAINING RINGS—PYRIDIN AND ITS DERIVATIVES.

The **pyridin bases,** closely related to the vegetable alkaloids (p. 470) as well as to some of the basic substances formed during putrefaction, were first obtained from **oil of Dippel,** or **bone-oil** (*oleum animale*), an oil produced during the dry distillation of bones, horns, etc., and as a by-product in the manufacture of ammoniacal compounds from those sources. They also occur in coal-tar, naphtha, commercial ammonia, methylic spirit and fusel oil. They are formed synthetically: (1) By heating the aldehyde-ammonias (p. 360) alone, or with aldehydes or ketones: (2) From pyrrole by the action of K or Na in presence of methylene iodid, etc. (3) By oxidation of hexahydropyridins, piperidins; also by other methods.

The pyridin bases are colorless liquids of peculiar, penetrating odor. The superior homologues are metameric with the anilins. They are strong triacid bases, and behave like tertiary monamins. Oxidizing agents do not attack pyridin, nor the nucleus of its superior homologues, but the lateral chains of the picolins, etc., are readily oxidized, with formation of **carbopyridic acids.** Reducing agents convert them into **piperidins** (p. 461). They react with several of the general reagents for the alkaloids (p. 472). The two most nearly characteristic properties of the pyridin bases are: (1) the formation of chloroplatinates such as $(C_5H_5N.HCl)_2PtCl_4$, which on boiling with water, lose two molecules of HCl to form "modified salts" such as $(C_5H_5N)_2PtCl_4$ (Anderson's reaction), and, (2) the

formation of crystalline addition products, alkyl-pyridinium iodids, such as $C_5H_5N\langle^{CH_3}_{I}$ on contact of their alcoholic solutions with alkyl iodids.

Pyridin—$HC\langle^{CH:CH}_{CH.CH}\rangle N$—is obtained from oil of Dippel, or from piperidin. It boils at 115° (239° F.), mixes with water in all proportions, is strongly alkaline in reaction. Its hydrochlorid is crystalline, but deliquescent. Its chloroplatinate fuses at 240° (464° F.). When reduced by sodium and alcohol, it forms piperidin, or hexahydropyridin; and when reduced by hydriodic acid, normal pentane, $CH_3.CH_2.CH_2.CH_2.CH_3$.

Pyridin Homologues—Alkyl Pyridins—are substitution products containing alkyl groups for H. Owing to the inequality in value of the several C atoms of pyridin (p. 454), the number of substituted derivatives is greater than with benzene. There are three monosubstituted derivatives, six each of the bi- and tri-substituted, three tetra-, and one penta-substituted.

Methyl-pyridins—Picolins—$C_5H_4N(CH_3)$—The three picolins, $\alpha$, $\beta$ and $\gamma$, exist in oil of Dippel, and have been formed synthetically. Their b. p.'s are 130°, 143°, and 144°.

Lutidins—Three ethyl pyridins, $C_5H_4N(C_2H_5)$, are known, $\alpha$, b.p. 148°; $\beta$, b.p. 166°; and $\gamma$, b.p. 165°. Of the six possible dimethyl-pyridins, $C_5H_3N(CH_3)_2$, four are known, three of which exist in bone oil.

Collidins—$C_8H_{11}N$—There are twenty-two possible collidins, of which twelve are known. Of these several are products of decomposition of vegetable alkaloids, or exist in oil of Dippel, or are produced during putrefaction. Conyrin, a basic substance produced by boiling coniïn (p. 472) with $ZnCl_2$, is $\alpha$-propyl-pyridin. $\beta$-propyl-pyridin is produced from nicotin by passing its vapor through a red-hot tube. Aldehydin is 1, 4-methyl-ethyl-pyridin, formed by heating aldehyde-ammonia in alcoholic solution to 120° (248° F.), and from other aldehyde compounds; and exists also in the products of rectification of alcohol. An oily ptomaïn produced during putrefaction of gelatin in presence of pancreas is a collidin of undetermined constitution.

Parvolins—$C_9H_{13}N$.—Theory indicates the existence of 57 parvolins, of which five are known. One of these is a ptomaïn, produced during putrefaction of mackerel and of horse-flesh. It is an oily substance, slightly soluble in water, having, when fresh, the odor of hawthorn-blossoms, but becoming brown and resinous on exposure to air.

Coridins—$C_{10}H_{15}N$.—One of the coridins has been obtained as a product of putrefaction of fibrin and of jellyfish during several

months. It is an alkaline oil, which has a poisonous action similar to that of curari. The pyridin bases in general exert a paralyzing action upon the central, and to a less degree upon the peripheral nervous system. They are the antagonists of strychnin.

Besides the alkyl-pyridins a number of **phenyl-pyridins** (p. 469) and pyridins containing unsaturated lateral chains, such as **vinyl-pyridin**, $C_5H_4N(C_2H_3)$, are known.

**Pyridin Carboxylic Acids.** — These acids, which bear the same relation to pyridin that the benzoic, phthalic, etc., acids bear to benzene, are formed by oxidation of the alkyl-pyridins. As most of the alkaloids contain pyridin nuclei with lateral chains, they yield pyridin-carboxylic acids upon sufficient oxidation. Thus **pyridin-β-monocarboxylic acid, or β-picolinic acid**, $C_5H_4N(COOH)_{(2)}$, is **nicotinic acid**, formed by oxidation of nicotin, of pilocarpin, as well as of β-picolin. The α acid is formed by oxidation of α-picolin. The γ acid, **isonicotinic acid**, is formed by oxidation of 3-picolin, and of many of its derivatives. **Pyridin-1, 2-dicarboxylic acid**, $C_5H_3N(COOH)_{2(1,2)}$, is **quinolinic acid**, formed by oxidation of quinolin, and **pyridin-2, 3-dicarboxylic acid** is **cinchomeronic acid**, formed by oxidation of cinchonin, cinchonidin and quinin.

**Hydropyridins — Piperidins** — are compounds produced from the pyridins by the action of nascent hydrogen. **Dihydropyridins** and **tetrahydropyridins** are known, the latter known as **piperideïns**, but by far the most important of the group is

**Piperidin — Hexahydropyridin** — $H_2C\begin{matrix}CH_2.CH_2\\CH_2.CH_2\end{matrix}NH$ — which is produced by saponification of **piperin** (p. 474) by heating with alcoholic KHO, and is also formed by reduction of pyridin, or by heating pentamethylene-diamin hydrochlorid. It is a colorless liquid; b. p. 106° (222.8° F.); having an odor like that of pepper; readily soluble in water and in alcohol. Oxidizing agents rupture the piperidin ring, with formation of aliphatic compounds. When heated with methyl iodid is converted into **methylpiperidin hydroiodid**, $H_2C\begin{matrix}CH_2.CH_2\\CH_2.CH_2\end{matrix}N\begin{matrix}HI\\CH_3\end{matrix}$.

Piperidin and methyl-piperidin are particularly of interest as being the nuclei of a number of vegetable alkaloids. Thus **coniïn** is **α propyl-piperidin**, and **tropin** and **ecgonin**, the basic nuclei of the atropic and cocain alkaloids, are derivatives of methyl-piperidin (see pp. 475, 477).

**Di-, tri-, and tetrazins** — are substances containing two, three, and four N atoms in the benzene ring. There are three diazins, three triazins, and three tetrazins, o-, m-, and p-, as the nitrogen atoms are placed in adjacent, symmetrical or unsymmetrical positions. Each of these forms a series of substituted derivatives.

**Ortho-diazin — Pyridazin** — $\begin{matrix}\text{N.CH:CH}\\ \|\quad\ |\\ \text{N.CH:CH}\end{matrix}$, **Meta-diazin—Pyrimidin**— $\begin{matrix}\text{N.CH:CH}\\ \|\quad\ |\\ \text{CH.N:CH}\end{matrix}$, and **Para-diazin — Pyrazin** — $\begin{matrix}\text{CH.N.CH}\\ \|\quad\ |\ \|\\ \text{CH.N.CH}\end{matrix}$ are known. The last-named is formed by oxidation of amido-acetaldehyde by distillation with mercuric chlorid solution: $2CHO.CH_2.NH_2+O=\begin{matrix}\text{CH.N.CH}\\ \|\quad\ |\ \|\\ \text{CH.N.CH}\end{matrix}+3H_2O$. It is also formed by heating piperazin with zinc dust. Pyrazin and its homologues are produced during fermentation, and exist in fusel-oils, and in commercial amylic alcohol. It is a solid; f. p. 55°; b. p. 115°; has the odor of heliotrope, and is strongly basic.

The three diazins form condensation products with benzene: the benzorthodiazins, $\begin{matrix}\text{CH:CH}\\ |\quad\ \diagdown\\ \text{N}\text{---}\text{N}\end{matrix}\diagup C_6H_4$, cinnolin, and $\begin{matrix}\text{N.CH}\\ \|\quad\ \diagdown\\ \text{N.CH}\end{matrix}\diagup C_6H_4$, phthalazin, and benzometadiazins, and benzoparadiazins.

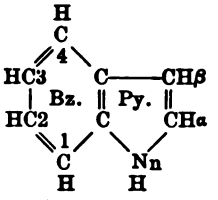
**Hexahydro-pyrazin—Piperazin—Diethylene Diamin**— $\begin{matrix}\text{CH}_2\text{.NH.CH}_2\\ |\qquad\ |\\ \text{CH}_2\text{.NH.CH}_2\end{matrix}$ —may be obtained by reduction of para-diazin, but is manufactured from diphenyl-diethylene diamin, $C_6H_5.N\begin{matrix}\diagup\text{CH}_2\text{.CH}_2\diagdown\\ \diagdown\text{CH}_2\text{.CH}_2\diagup\end{matrix}N.C_6H_5$, which is obtained by the action of ethylene bromid upon anilin. It crystallizes in colorless needles; f. p. 104°; b. p. 145°; soluble in water, and deliquescent. It is strongly alkaline and basic, and absorbs carbon dioxid from air. It forms a soluble compound with uric acid (p. 355), and is used medicinally as a solvent for uric acid in lithiasis.

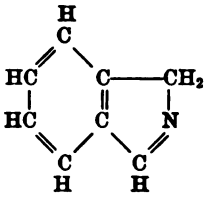
**Urazin — Diurea** — $\begin{matrix}\text{HN.CO.NH}\\ |\qquad\ |\\ \text{HN.CO.NH}\end{matrix}$ —is the diketonic derivative of symmetrical tetrazin (p. 353).

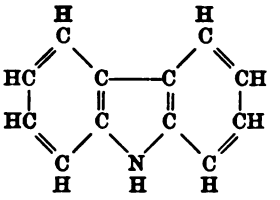
## B. CONDENSED HETEROCYCLIC COMPOUNDS.

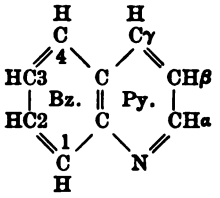
These compounds, which are more numerous than the corresponding carbocyclic compounds (p. 438), may be considered as being derived from the latter by substitution of N for methine, =CH—, or of O, S, or NH in a bivalent position, or, as in the case of iso-indole (p. 463), by substitution and modification of internal linkage. The number of these substances is still further increased by the existence of four ringed-compounds, such as the anthraquinolins and indigo-blue (p. 466). The formulæ on the following page are those of some of the nitrogen derivatives, in which indole and isoindole may be considered as derived from indene (p. 438): carbazole from fluorene; quinolin, iso-quinolin and naphthydrin from naphthalene:

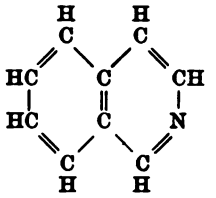
acridin and the anthrapyridins from anthracene; and phenanthridin from phenanthrene:

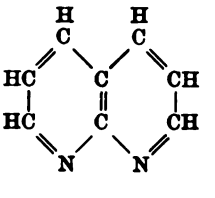

Benzo-pyrrole.
(Indole).

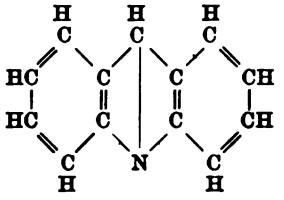

Iso-indole.

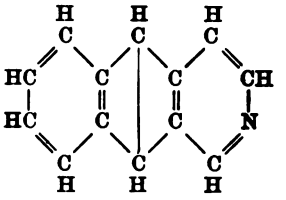

Diphenylene-imid.
(Carbazole).

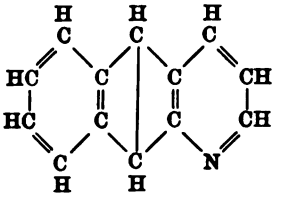

Benzo-pyridin.
(Quinolin).

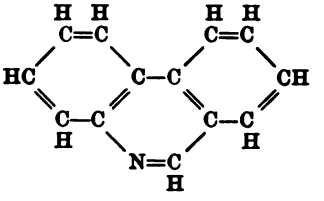

Iso-quinolin.


Naphthydrin.


Acridin.


α-Anthrapyridin.


β-Anthrapyridin.


Phenanthridin.

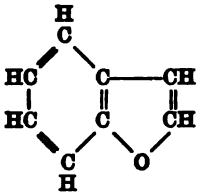
## CONDENSED NUCLEI CONTAINING OXYGEN OR SULFUR MEMBERS.

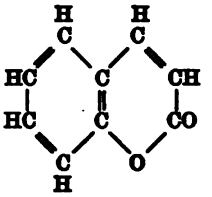
Of these we will consider only a few of the oxygen compounds:

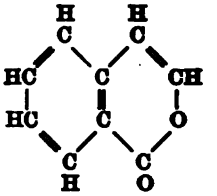
**Coumarone — Benzofurfurane** — (formula p. 464) — is formed by the action of KHO upon the coumarins, and is the parent substance of two series of substitution derivatives, α and β.

**Coumarin**, and **isocoumarin** and their alkyl and phenolic deriva-

tives, e.g. umbelliferone, æsculetin, daphnetin, hesperetin, exist in different vegetables (pp. 410, 413). Coumarin is the odorous principle of Tonka beans, and also exists in a variety of other vegetables. It is formed by the action of acetic anhydrid and sodium acetate upon salicylic aldehyde. It forms crystalline needles; f.p. 67°; soluble in water, alcohol and ether. Coumarin and isocoumarin are benzo-derivatives of α-pyrone (p. 458):


Coumarone.


Coumarin.


Iso-coumarin.

Benzo- and dibenzo-γ-pyrones, the latter called xanthones, exist in several natural yellow dyes of vegetable origin, as from quercetin and chrysin (p. 413).

## CONDENSED NUCLEI CONTAINING A NITROGEN MEMBER.

### BENZOPYRROLE AND ITS DERIVATIVES — INDIGO COMPOUNDS.

Indole — Benzopyrrole — (formula p. 463) — is produced: (1) by distilling oxindole over zinc-dust; (2) by heating o-nitro-cinnamic acid (p. 403) with potash and iron filings, or by similar reduction of other unsaturated o-nitro substitution products of benzene (3) by the interaction of calcium formate and phenylglycocoll (p. 424). It is one of the products of putrefaction of the proteins by anærobic bacteria, and is formed in the intestine during pancreatic digestion of those substances. It is partly eliminated with the fæces and partly reabsorbed, appearing in the urine in sulfoconjugate combination. It crystallizes in large, shining, colorless plates, having the disagreeable odor of naphthylamin. It is a weak base, and its salts are decomposed by boiling water. Its aqueous solution, acidulated with HCl, is colored rose-red by $KNO_2$. By fusion with KHO it yields anilin. It gives the "pine-shaving reaction" (p. 455). It forms a compound, crystallizing in red needles, with picric acid.

Indole Homologues — Derivatives of indole are produced by substitution either in the benzene or in the pyrrole ring. The positions are distinguished as Bz. 1, 2, 3, 4 and Py.*n*, α, and β (see formula p. 463). The alkyl indoles, the superior homologues of indole, are formed: (1) by heating anilin with compounds containing the group $CO.CH_2Cl$. Thus chloracetone and anilin yield α-methyl-

**indole**: $CH_2Cl.CO.CH_3+C_6H_5.NH_2=C_6H_4\langle^{CH}_{NH}\rangle C.CH_3+HCl+H_2O$; (2) by heating the phenylhydrazones (p. 429) of the ketones, aldehydes or ketone acids with $ZnCl_2$. Thus *n*, α-**dimethylindole** is obtained from acetone-phenyl-methyl-hydrazone: $C_6H_5.N(CH_3).N:C\langle^{CH_3}_{CH_3}=C_6H_4\langle^{CH}_{N(CH_3)}\rangle C.CH_3+NH_3$.

The best known alkyl indoles are those in which the alkyl group is in the pyrrole ring. They dissolve in concentrated acids, and are precipitated unaltered from the solutions by dilution with water. Fused with KHO, they yield potassium salts of **indole-carboxylic acids.** Their hydrogen may be replaced by acidyls or by the diazo group. They give the "pine-shaving reaction," and form red, crystalline compounds with picric acid.

**β-Methyl-indole—Skatole**—$C_6H_4\langle^{C(CH_3)}_{NH}\rangle CH$—exists in fæces, in which it exceeds the indole in amount. It is formed during putrefaction of the proteins, or by the action upon them of KHO in fusion; also by the reduction of indigo. It is best obtained synthetically by heating propidene-phenylhydrazone with zinc chlorid: $C_6H_5.NH.N:CH.CH_2.CH_3=C_6H_4\langle^{C(CH_3)}_{NH}\rangle CH+NH_3$. It crystallizes in brilliant plates; f.p. 95° (203° F.); insoluble in water, soluble in alcohol and in ether; distils with vapor of water; has a strong fæcal odor. Its solution in concentrated HCl is violet. Its $H_2SO_4$ solution is colored deep purple when heated. Skatole, like indole, is in part reabsorbed from the intestine, and appears in the urine, combined with sulfuric and glucuronic acids.

**β-Methyl-indole-α-carboxylic Acid**—$C_6H_4\langle^{C(CH_3)}_{NH}\rangle C.COOH$—f.p. 165°; is a product of putrefaction, and also occurs in normal urine. It produces an intense violet color with HCl and dilute $Fe_2Cl_6$ solution. **Skatole-acetic acid**—$C_3H_4\langle^{C(CH_3)}_{NH}\rangle C.CH_2.COOH$—is also produced during putrefaction.

**Iso-indole**—(formula, p. 463)—is formed by the action of alcoholic ammonia upon brom-acetophenone (p. 400). It crystallizes in colorless, silky plates; f. p. 195°; insoluble in water, soluble in alcohol, ether and benzene.

**Indoxyl—β-Oxyindole**—$C_6H_4\langle^{C(OH)}_{NH}\rangle CH$—not to be confounded with oxindole (p. 466), is a phenolic derivative of indole, obtained from indigo-blue by fusion with KHO without contact of air; or from its α-carboxylic acid, **indoxylic acid.** It is a very unstable, oily substance, soluble in water, and readily oxidized to indigo-blue (below). It readily combines with sulfuric acid or the sulfates to form **indoxyl-sulfuric acid**, $C_6H_4\langle^{C—O—S:O_2}_{NH—CH\ OH}$, which is

the uroxanthin, or urinary indican, existing in the urine, and formed from indole. Acids decompose it, with formation of indoxyl, which is converted into indigo-blue by $Fe_2Cl_6$ (see Urine).

**Oxindole** — $C_6H_4\langle^{CH_2}_{NH}\rangle CO$ — the lactam of o-amido-phenyl acetic acid (p. 424), is obtained from dioxindole by reduction with sodium amalgam in acid solution; or by reduction of o-nitrophenyl-acetic acid. It crystallizes in easily soluble, colorless needles; f. p. 120°. In moist air it oxidizes to dioxindole. It reduces ammoniacal silver nitrate solution. It combines with acids and bases.

**Dioxindole—Hydrindic Acid**— $C_6H_4\langle^{CH(OH)}_{NH}\rangle CO$ — is the lactam o-amido-mandelic acid (p. 424), and is formed by the action of Na on isatin suspended in water. It forms yellow prisms, soluble in water, and combines with acids and bases.

**Isatin** — $C_6H_4\langle^{CO}_{NH}\rangle CO$ — the lactam of o-amido-benzoyl-formic acid (p. 424), is formed by oxidation of indigo-blue by $HNO_3$; by oxidation of oxindole or of dioxindole; and by other methods. It crystallizes in shining, transparent, red-brown prisms, odorless, sparingly soluble in water, readily soluble in alcohol. On further oxidation it yields **isatoic acid**, $C_6H_4\langle^{CO}_{N.COOH}$. With hydroxylamin it forms **isatoxim**, $C_6H_4\langle^{C=NOH}_{N=COH}$, which is also formed by the action of nitrous acid upon oxindole.

**Indigo-blue**—**Indigotin**— $C_6H_4\langle^{CO}_{NH}\rangle C:C\langle^{CO}_{NH}\rangle C_6H_4$ — constitutes the greater part of commercial indigo. It does not exist preformed in nature, but many plants, particularly *Indigotifera tinctoria* and *Isatis tinctoria*, contain a yellow glucosid, indican (p. 413), which on heating with dilute acids, or probably by enzymic action on exposure to air in presence of water, is decomposed into a sugar and indigo-blue. Commercial indigo contains 20 to 90 per cent. of indigo-blue, which may be separated, nearly pure, by cautious sublimation. It is formed in several reactions, e. g., by oxidation of indoxyl by $Fe_2Cl_6$ and HCl; from o-nitro-cinnamic acid by two methods; by fusing phenyl-glycocoll (p. 424) with KHO; or by heating o-nitro-acetophenone (p. 400) with zinc dust. It forms purple-red, metallic, shining prisms or plates, odorless, tasteless, neutral, soluble in hot anilin, hot oil of turpentine, and melted paraffin, insoluble in the usual solvents. When heated it is in part converted into a dark red vapor, and partly decomposed into anilin and other products. In the presence of aqueous alkaline solutions, reducing agents convert indigo-blue into **indigo-white**, or **di-indoxyl**, $C_6H_4\langle^{C(OH)}_{NH}\rangle C—C\langle^{C(OH)}_{NH}\rangle C_6H_4$, which dissolves in the

alkali. This substance absorbs oxygen from the air rapidly, with regeneration of indigo-blue. In absence of air it may be precipitated from its alkaline solution by HCl, as a white, crystalline powder, insoluble in water, but soluble in alcohol and ether, forming yellow solutions. When oxidized, as by warming with dilute $HNO_3$, indigo-blue is converted into isatin, whose dilute solutions are also yellow. Hence the decoloration of indigo-blue solution is utilized as a test both for oxidizing ($HNO_3$) and for reducing (Mulder-Neubauer test for glucose) substances.

**Indigo-sulfonic Acids.**—Indigo-blue dissolves slowly in concentrated sulfuric acid, to a green solution, from which water precipitates a blue powder, soluble in water, but insoluble in dilute acids. This is **indigo-monosulfonic** or **phoenicin-sulfonic acid**, $C_{16}H_9N_2O_2.SO_3H$, which forms purple-red salts, soluble in water. With fuming (Nordhausen) sulfuric acid, **indigo-disulfonic, sulfindylic,** or **sulfindigotic acid**, $C_{16}H_8N_2O_2(SO_3H)_2$, is formed, whose K and Na salts are also soluble in water, and are met with in commerce as pastes called **indigo-carmine.**

**Dibenzo-pyrrole—Diphenyl-imid—Carbazole**—(formula p. 463)—exists in crude anthracene, and is formed by passing diphenylamin through a red-hot tube, and from other diphenyl derivatives. It is a crystalline solid; f. p. 238°; soluble in alcohol and in toluene. It is a weak base, gives the pine-shaving reaction, and the blue color with isatin and $H_2SO_4$, and forms a picrate fusible at 182°.

## QUINOLIN AND ISO-QUINOLIN AND THEIR DERIVATIVES.

The **quinolin,** or **benzo-pyridin bases** accompany the pyridin bases (p. 459) in bone-oil, and like those substances, are closely related to the vegetable alkaloids. Quinolin, the parent substance of the group, was first obtained by distilling quinin and cinchonin with lime.

Chemically the quinolins are also related to the naphthalenes (p. 452), and are formed by similar synthetic methods. Thus quinolin is formed from allyl-anilin: $C_6H_5.NH.CH_2.CH:CH_2 = C_6H_4\langle^{N\ :CH}_{CH:CH}+2H_2$, in the same manner as naphthalene is formed from phenyl-butylene (p. 440). Quinolin and its derivatives may also be produced synthetically: (1) From o-amido-benzenic compounds containing an oxygen atom in the second lateral chain. Thus o-amido-benzoic aldehyde and acetone yield α-methyl-quinolin: $C_6H_4\langle^{CHO_{(1)}}_{NH_{2\ (2)}} + CH_3.CO.CH_3 = C_6H_4\langle^{CH:CH}_{N\ :C(CH_3)}$ + $2H_2O$. (2) By heating the anilins with glycerol and $H_2SO_4$, in presence of an oxidizing

agent, such as nitro-benzene: $C_6H_5.NH_2+CH_2OH.CHOH.CH_2OH=$ $C_6H_4\begin{matrix}CH:CH\\|\\N\ :CH\end{matrix}+3H_2O+H_2$. (3) By the action of aldehydes upon anilins in presence of $H_2SO_4$ or HCl. Thus α-methyl-quinolin is obtained from anilin and acetic aldehyde: $C_6H_5.NH_2+2CHO.CH_3=$ $C_6H_4\begin{matrix}CH:CH\\|\\N\ :C(CH_3)\end{matrix}+2H_2O+H_2$.

The quinolin bases are liquids of penetrating odor, sparingly soluble in water, readily soluble in alcohol and in ether. They are strong triacid bases, and form salts and ammonium-like compounds.

**Quinolin**—$C_6H_4\begin{matrix}CH:CH\\|\\N\ :CH\end{matrix}$—is a mobile liquid; b. p. 238° (460.4° F.); becoming rapidly brown on exposure to air; has an intensely acrid and bitter taste, and an odor somewhat like that of bitter almonds; sparingly soluble in water, readily soluble in alcohol and ether. Its dichromate crystallizes in yellow needles; f. p. 165°; very sparingly soluble in water.

**Quinolin Homologues**—Quinolin is the nucleus of a vast number of products of substitution, among which are many isomeres, due to differences in orientation, according as the substitution occurs in the o-, m-, or p- position in the benzene ring, or in the α, β, or γ position in the pyridin ring (see formula, p. 463). Thus there are seven **methyl-quinolins**, or **lepidins**, etc.

Quinolin is of medical interest chiefly in connection with the vegetable alkaloids of which it is the nucleus (p. 478). Certain synthetic basic substances containing the quinolin nucleus have also been used in medicine, in saline combination, as antiperiodics and antipyretics. Among these are **thallin**, **ethyl-thallin** and **kairin**.

**α-Oxyquinolin—Carbostyril**—$C_6H_4\begin{matrix}CH:CH\\|\\N\ :C.OH\end{matrix}$—is the lactam of o-amido-cinnamic acid, formed by reduction of o-nitro-cinnamic ester.

**Iso-quinolin**—$C_6H_4\begin{matrix}CH:CH\\|\\CH:N\end{matrix}$—differs from quinolin in that the attachment of the benzene and the pyridin rings is by the β and γ positions of the latter in iso-quinolin, and by the α and β positions in quinolin (see formulæ, p. 463). It accompanies quinolin in coal-tar, and is the nucleus of the opium alkaloids (p. 483). It resembles quinolin in its properties. F. p. 23°; b. p. 240.5°.

**Hydroquinolins.**—Compounds corresponding to **dihydroquinolins** are known. **Tetrahydroquinolins** are formed, by hydration of the pyridin ring, by the action of nascent hydrogen on quinolins. **Decahydroquinolin**, $C_9H_{18}N$, corresponding to piperidin (p. 461), is formed by heating quinolin with hydriodic acid and phosphorus.

## C. PHENYL-PYRIDYL, DIPYRIDYL, AND PYRIDYL-PYRROLE COMPOUNDS.

These compounds (p. 453) contain two nuclei, one at least heterocyclic, united together by loss of two hydrogen atoms.

**Phenyl-pyridyls, or phenyl-pyridins** (p. 461) consist of one or more phenyl groups substituted in pyridin, **γ-Phenyl-pyridyl,** $N\langle\begin{smallmatrix}CH{=}CH\\CH{-}CH\end{smallmatrix}\rangle C{-}C\langle\begin{smallmatrix}CH{=}CH\\CH{-}CH\end{smallmatrix}\rangle CH$, as well as the α and β compounds, and **diphenyl- and tetraphenyl-pyridins,** are known.

**γ, γ-Dipyridyl**—$N\langle\begin{smallmatrix}CH{=}CH\\CH{-}CH\end{smallmatrix}\rangle C{-}C\langle\begin{smallmatrix}CH{=}CH\\CH{-}CH\end{smallmatrix}\rangle N$—is formed by the action of sodium upon pyridin. It forms colorless needles; f. p. 114°; which yield isonicotinic acid (p. 461) on oxidation. The α-β and β-β dipyridyls are formed by oxidation of the phenanthrolins, and both yield nicotinic acid on oxidation. A fourth, probably α-α, is formed by passing vapor of pyridin through a red-hot tube. The dipyridyls take up nascent hydrogen to form substances, $C_{10}H_{14}N_2$, isomeric with nicotin, and resembling that alkaloid (p. 473) closely in chemical properties and in physiological action. The one obtained from β-β dipyridyl is a very soluble and highly poisonous liquid, called **nicotidin.** That from γ-γ dipyridyl is a crystalline solid, soluble in water, less actively poisonous than nicotin, and called **isonicotin.**

The **pyridyl-pyrroles** are formed by union of a pyridin and a pyrrole ring, as the dipyridins are formed by union of two pyridin rings. **α-Pyridin-β-pyrrole,** $HC\langle\begin{smallmatrix}CH{=}CH\\CH{-}\ N\end{smallmatrix}\rangle C{-}C\langle\begin{smallmatrix}CH{-}NH\\CH{=}CH\end{smallmatrix}\rangle$, constitutes the nucleus of nicotin (p. 474). It is a crystalline solid; f. p. 72°.

## ALKALOIDS.

Until the constitution of all the substances grouped under this term shall have been determined, the limitations of the application of the name can be only provisional. It was first applied to the few alkali-like substances first obtained from vegetable products, the vegetable bases morphin, narcotin, veratrin, strychnin. Afterwards its application was extended, and at the same time made more precise, to include organic, nitrogenized substances, alkaline in reaction, and capable of combining with acids to form salts in the same way as does ammonia. This limitation is, however, too broad, as it classes the aliphatic amins, and other similar bodies, with the true alkaloids, which are cyclic. All substances generally classed as alkaloids, whose

constitution has been determined, contain at least one nitrogen-containing heterocyclic ring, except theobromin and caffeïn, which are not true alkaloids, but purin bases (p. 358). Almost all alkaloids of known constitution contain the pyridin ring, more or less modified by hydrogenation, either alone or in quinolin or isoquinolin. Therefore, until recently, alkaloids were considered to be: basic substances containing the pyridin ring. But the hygrins, alkaloids existing in coca leaves, are derivatives, not of pyridin, but of pyrrolidin (p. 456), a five-membered nucleus. So far as is now known, no alkaloid contains more than one nitrogen atom in one and the same ring. Therefore, provisionally, it may be stated that the alkaloids are basic substances derived from heterocyclic nuclei containing but one nitrogen atom in each nucleus. Under this definition pyridin and quinolin and their homologues are alkaloids, as well as indole, and other basic pyrrole compounds.

Some of the alkaloids, nicotin, coniïn, sparteïn and arecolin are liquid, volatile, and contain C, N and H. Most of them, to the number of more than a hundred, are solid, crystalline, only partially volatile without decomposition, if at all, and contain C, N, H and O. Most of the alkaloids are very sparingly soluble in water, although some are readily soluble; but soluble in alcohol, ether, petroleum-ether, chloroform, benzene or amylic alcohol. Their salts, on the other hand, are, for the most part, soluble in water, but insoluble in the other solvents mentioned, except alcohol, in which they are soluble. They are laevogyrous, except quinidin, cinchonin, coniïn, narcotin and pilocarpin, which are dextrogyrous. Usually their rotary power is diminished by combination with acids, although with quinin the reverse is the case. Free narcotin is laevogyrous, its salts are dextrogyrous. Most of the alkaloids are bitter in taste, and alkaline in reaction.

The naming of the salts of the alkaloids has been the subject of no little discussion. In obedience to the rules of orthography adopted (see Appendix) the names of the alkaloids are made to terminate in *in*, although in non-chemical writings the termination *ine* is still usual, and the older termination *ia* is occasionally met with. As most of the alkaloids are tertiary amins and some secondary amins, they combine with acids in the same manner that ammonia does, that is, without elimination of water or of hydrogen, and by change of the nitrogen valence from trivalent to quinquivalent:

$$2H_3 : N + H_2SO_4 = (H_3 : N:)_2 \begin{matrix} H_2 \\ SO_4 \end{matrix}$$

Ammon*ia*. Sulfuric acid. Ammon*ium* sulfate.

$$2[(C_{17}H_{19}O_3) : N] + H_2SO_4 = [(C_{17}H_{19}O_3) : N:]_2 \begin{matrix} H_2 \\ SO_4 \end{matrix}$$

Morph*ia*. Sulfuric acid. Morph*ium* sulfate.

Therefore these salts do not contain morphin, $C_{17}H_{19}O_3N'''$, as a substitute for the hydrogen of the acid, but the hypothetical morphium $(C_{17}H_{20}O_3N^v)'$, as the ammoniacal salts are not salts of ammonia, $NH_3$, but of ammonium, $NH_4$. The compounds formed by the union of morphin and other alkaloids with the hydracids, HCl, HBr, HI, may properly and conveniently be referred to as morphin hydrochlorid (not hydrochlorate) hydrobromid, hydroiodid, etc., they being considered, not as salts of those acids, but as compounds in which one of the valences of the quinquivalent nitrogen atom is satisfied by hydrogen and another by chlorin.

Many of the alkaloids behave like esters, and are hydrolyzed by baryta or the caustic alkalies, or by mineral acids, into two components, one a base, the other an acid, the latter usually cyclic and nitrogenous. On the other hand, concentrated HCl removes $H_2O$ from those alkaloids containing more than one hydroxyl, converting them into apo-alkaloids, as morphin is converted into apomorphin. Other alkaloids, containing methoxyl groups ($OCH_3$), when acted upon by concentrated HCl, are modified by replacement of OH for the methoxyl groups. Reducing agents form hydro-bases, as piperidin is derived from pyridin. Distillation with zinc-dust causes removal of the lateral chains from the oxygen-containing alkaloids, with liberation of pyridin or quinolin. Oxidizing agents form carboxylic acids, or decompose the alkaloid into an acid and a base, or cause the union of two molecules of the alkaloid with loss of hydrogen.

**Separation of Alkaloids from Organic Mixtures.**—The separation of an alkaloid from an organic mixture (contents of stomach, viscera, etc.) in a condition of purity sufficient to permit of its identification, is one of the most difficult tasks of the toxicologist, and not to be attempted in a case liable to be the subject of legal inquiry except by one thoroughly competent. The processes usually followed are modifications of that originally used by Stas, of which the most exhaustive is the method of Dragendorff. They depend upon differences in the solubilities of the several alkaloids and of their salts in water or alcohol, and in various solvents immiscible with water. The alkaloid is first extracted as a tartrate, sulfate or hydrochlorid by water or alcohol, acidulated with the appropriate acid, and the extract purified to a clear, acid, watery solution. This acid solution is then successively shaken with the immiscible solvents, such as ether, petroleum-ether, benzene, chloroform, amylic alcohol and acetic ether, the solvents being separated from the aqueous solution, and each evaporated by itself. During this treatment the alkaloids are held in the aqueous solution, while the other solvents extract impurities and certain glucosidal and acid poisons. The watery solution is now

rendered alkaline, which causes liberation of the alkaloid from its saline combination, and is again successively agitated with the immiscible solvents named, they being each individually separated from the aqueous liquid and evaporated. Each solvent extracts those alkaloids which it is capable of dissolving, and they are sought for by the suitable tests in the appropriate residues. Thus strychnin is extracted by benzene, and morphin by amylic alcohol. The details of the process, which are quite elaborate, must be carefully observed, and the student is referred to special treatises upon the subject.

**General Reactions of the Alkaloids.**—A great number of "general reagents" for alkaloids have been suggested, of which only the more important can be here mentioned:

***Potash***, ***soda***, ***ammonia***, ***lime***, ***baryta*** and ***magnesia*** precipitate the alkaloids from solutions of their salts.

***Phosphomolybdic acid*** forms a precipitate which is bright-yellow with anilin, morphin, veratrin, aconitin, emetin, atropin, hyoscyamin, theïn, theobromin, coniïn and nicotin; brownish-yellow with narcotin, codeïn, and piperin; yellowish-white with quinin, cinchonin and strychnin; yolk-yellow with brucin (DeVry's, or Sonnenschein's reagent).

***Potassium iodhydrargyrate*** gives a yellowish precipitate with alkaloidal solutions which are acid, neutral or faintly alkaline in reaction (Mayer's reagent).

**Classification of the Alkaloids.**—The alkaloids of known, or partially known constitution, can be classified according to the nuclei which they contain:

A. *Pyrrole alkaloids.*—The hygrins are the only alkaloids now known of this group.

B. *Pyridin alkaloids*—including trigonellin, pilocarpin, arecolin, coniïn, nicotin, piperin, the atropic alkaloids, cocaïn, pelletierin, sparteïn, cytisin and their derivatives.

C. *Quinolin alkaloids*—including the cinchona and strychnos alkaloids.

D. *Isoquinolin alkaloids*—including the opium, hydrastis, berberis and corydalis alkaloids.

E. *Alkaloids of undetermined constitution.*

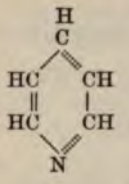
## PYRIDIN ALKALOIDS.

**Coniïn**—$C_8H_{17}N$—is the most simply constituted of the natural vegetable alkaloids, and was the first to be produced synthetically. It exists in *Conium maculatum*, in which it is accompanied by two other alkaloids, **methyl-coniïn**, $C_8H_{16}N(CH_3)$, and **conhydrin**, $C_9H_{17}NO$, the former a volatile liquid, the latter a crystalline solid.

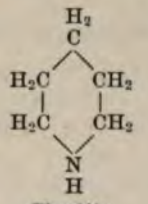
Coniïn is a colorless, oily liquid; has an acrid taste and a disagreeable, penetrating odor; sp. gr. 0.878; can be distilled when protected from air; boils at 212° (413.6° F.). Exposed to air it resinifies. It is very sparingly soluble in water, but is more soluble in cold than in hot water; soluble in all proportions in alcohol, soluble in six volumes of ether, very soluble in fixed and volatile oils.

Its vapor at ordinary temperatures forms a white cloud when in contact with a glass rod moistened with HCl, as does $NH_3$. It forms salts which crystallize with difficulty. Chlorin and bromin combine with it to form crystallizable compounds; iodin in alcoholic solution forms a brown precipitate in alcoholic solutions of coniïn, which is soluble without color in an excess. Ethyl and methyl iodids combine with it to form ethyl- and methyl-coniïn hydriodids.

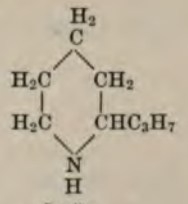
It has been obtained synthetically from α-picolin by reactions which show it to be **α-propyl piperidin.** The relations of pyridin, piperidin, and coniïn are shown by the following formulæ:



Pyridin.



Piperidin.



Coniïn.

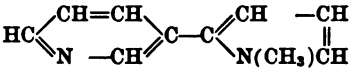
Analytical Characters.—(1.) With dry HCl gas it turns reddish-purple, and then dark-blue. (2) Aqueous HCl of sp. gr. 1.12 evaporated from coniïn leaves a green-blue, crystalline mass. (3) With iodic acid: a white ppt. from alcoholic solutions. (4) With $H_2SO_4$ and evaporation of the acid: a red color, changing to green, and an odor of butyric acid. (5) When mixed with commercial nitrobenzene a fine blue color is produced, changing to red and yellow.

**Paraconiïn**—$C_8H_{15}N$—is a synthetical product closely resembling coniïn, obtained by first allowing butyric aldehyde and an alcoholic solution of ammonia to remain some months in contact at 30° (86° F.), when dibutyraldin is formed: $2(C_4H_8O)+NH_3=C_8H_{17}NO+H_2O$. The dibutyraldin thus obtained is then heated under pressure to 150°–180° (302°–356° F.), when it loses water, and forms paraconiïn: $C_8H_{17}NO=C_8H_{15}N+H_2O$. A synthesis which, in connection with the decompositions of paraconiïn, shows its rational formula to be $\overset{(C_4H_7)'_2}{\underset{H}{\diagdown\!\diagup}}N$.

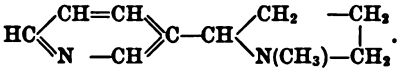
**Nicotin**—$C_{10}H_{14}N_2$—exists in tobacco in the proportion of 2–8 per cent. It is a colorless, oily liquid, which turns brown on exposure

to air, has a burning, caustic taste, and a disagreeable, penetrating odor. It distils at 250° (392° F.); burns with a luminous flame; sp. gr. 1.027 at 15° (59° F.); is very soluble in water, alcohol, the fatty oils, and ether. The last-named fluid removes it from its aqueous solution when the two are shaken together. It absorbs water rapidly from moist air. Its salts are deliquescent, and crystallize with difficulty.

The oxidation of nicotin produces nicotinic, or $\beta$ monocarbopyridic, acid (p. 461). When distilled with zinc chlorid and lime it yields pyrrole, ammonia, methylamin, hydrogen, and pyridin bases. When heated to 250° (482° F.) it yields a collidin along with other products. By limited oxidation it produces a substance, $C_{10}H_{10}N_2$, formerly considered as isodipyridin, but shown to be $\beta$-pyridin-n-methyl-a-pyrrole,



of which nicotin is the tetrahydro, or pyrrolidin derivative—

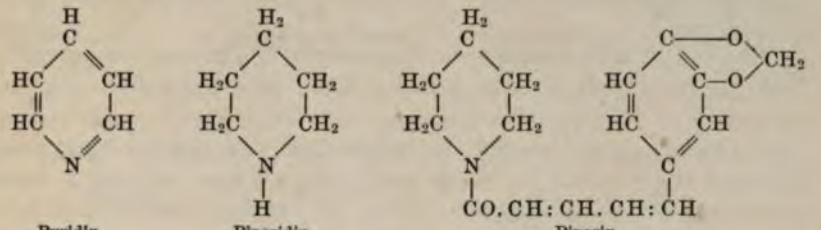


Analytical Characters.—(1) Its ethereal solution, added to an ethereal solution of iodin, separates a reddish-brown, resinoid oil, which gradually becomes crystalline. (2) With HCl, a violet color. (3) With $HNO_3$, an orange color.

Toxicology.—Nicotin is a very active poison. The free alkaloid is probably capable of causing death in doses of two to three drops. It was the first alkaloid to be separated from the cadaver in a case of homicide. Most cases of poisoning from nicotin are due to tobacco, frequently resulting from its use in enemata. When administered to dogs in doses of two to four drops, its effects begin within half a minute to two minutes, and death ensues within one to five minutes. In the human subject tobacco or its decoction causes nausea, vertigo, dilatation of the pupils, vomiting, syncope, diminution of the rapidity and force of the heart. With large doses there are no subjective symptoms, the victim falls unconscious instantly, and dies within five minutes, without convulsions, and with very few or only one deep sighing respiratory act.

**Piperin**—$C_{17}H_{19}NO_3$—an alkaloid occurring in black and white pepper, and isomeric with morphin, crystallizes in large prisms; f. p. 128°; almost insoluble in water, readily soluble in alcohol and in ether. It is a weak base, without alkaline reaction, and only forming very unstable salts with concentrated acids. It is one of the

alkaloids whose complete synthesis has been accomplished, and is one of the "ester-alkaloids" most directly derived from pyridin. When piperin is heated with alcoholic soda, it is hydrolysed into piperic acid, $C_{12}H_{10}O_4$ (p. 403), and piperidin. It is therefore **piperidin piperate, or piperidin 3, 4-methylene-dioxy-cinnamyl-acrylate:**

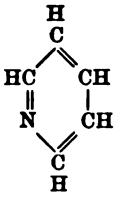



**Atropin—Atropina** (U. S.)—**Atropia** (Br.)—$C_{17}H_{23}NO_3$.—Belladonna, stramonium, hyoscyamus, and dubosia contain four alkaloids: *Atropin*, *hyoscyamin*, *hyoscin*, and *belladonin*. The first two are isomeric with each other, and possibly identical.

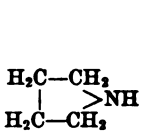
Atropin forms colorless, silky needles, which are sparingly soluble in cold water, more readily soluble in hot water, very soluble in chloroform. It is odorless, but has a disagreeable, persistent, bitter taste. It is distinctly alkaline, and neutralizes acids with formation of salts. One of these, the sulfate, is a white, crystalline powder, readily soluble in water, which is the form in which atropin is usually administered.

If atropin be acted upon by baryta at 60° (140° F.), or by caustic soda, or hydrochloric acid at 120°–130° (248°–266° F.) it is saponified, after the manner of an ester, into **tropic, or α-phenyl-hydracrylic acid** (p. 408), $C_6H_5.CH\langle^{COOH}_{CH_2OH}$, and a basic substance, **tropin**, $C_8H_{15}NO$. But if the action be prolonged the tropic acid is further decomposed into α-phenyl-acrylic, or atropic, and isatropic acids (p. 402). And if, during the action of HCl, the temperature rises to 180° (356° F.), the tropin loses water and is converted into **tropidin**, $C_8H_{13}N$.

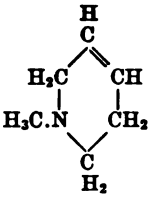
As the total syntheses of atropin and of tropin have not been accomplished, their structural formulæ are not definitely established; but, according to the most recent investigations, it is probable that tropidin consists of a pyrrolidin ring condensed with a tetrahydro-n-methyl-pyridin ring, having the group C-N-C in common; and that tropin is derived from tropidin by rupture of the double bond in the pyridin ring and hydration. It is established that atropin is tropin tropate. The relations of these bodies, according to these views, is shown by the following formulæ:



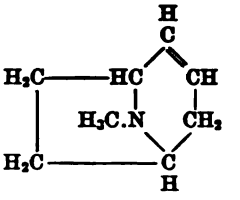
Pyridin.



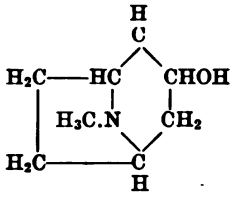
Pyrrolidin.



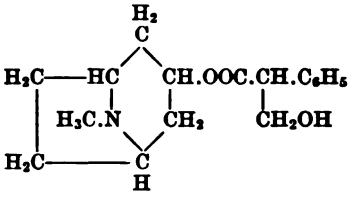
Tetrahydro-n-methyl pyridin.



Tropidin.



Tropin.



Tropin-α-phenyl-hydracrylate, or Atropin.

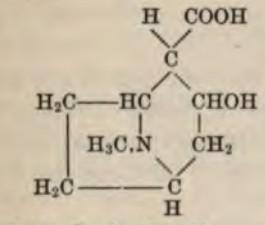
ANALYTICAL CHARACTERS.—(1) If a fragment of potassium dichromate be dissolved in a few drops of $H_2SO_4$, the mixture warmed, a fragment of atropin and a drop or two of $H_2O$ added, and the mixture stirred, an odor of orange-blossoms is developed. (2) A solution of atropin dropped upon the eye of a cat produces dilatation of the pupil. (3) The dry alkaloid (or salt) is moistened with fuming $HNO_3$ and the mixture dried on the water-bath. When cold, it is moistened with an alcoholic solution of KHO: a violet color, which changes to red (Vitali). (4) If a saturated solution of Br in HBr be added to a solution of atropin, a yellow precipitate is formed, which rapidly becomes crystalline, and which is insoluble in acetic acid, sparingly soluble in $H_2SO_4$ and HCl.

TOXICOLOGY.—The clinical history of atropic poisoning is divisible into two stages, the first one of delirium, in which the prominent symptoms are dryness of the throat, thirst, difficulty of deglutition and spasms upon swallowing liquids, face at first pale, afterwards highly reddened, pulse extremely rapid, eyes prominent, brilliant, with widely-dilated pupils, complete paralysis of accommodation, disturbances of vision, attacks of giddiness and vertigo, with severe headache, followed by delirium, occasionally silent or muttering, but usually violent, noisy and destructive, accompanied by the most fantastic delusions and hallucinations. Usually the urine is retained, and the body temperature is above the normal. The delirium gradually subsides, and the second stage, that of coma, is established, with slow, stertorous respiration, and gradually failing pulse, until death occurs from respiratory or cardiac paralysis, or sometimes in an attack of syncope during apparent amelioration. In some cases, the patient rapidly becomes comatose at the outset, and the symptoms of

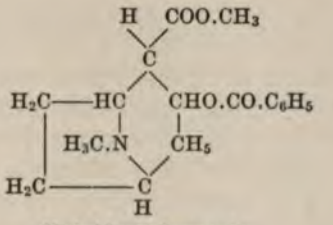
the first stage are manifested as the coma diminishes. The treatment should consist of lavage of the stomach, and morphin may be given cautiously during the period of violent excitement. In the second stage, the treatment is the same as in morphin poisoning. Pilocarpin may be given, in not too large doses, to stimulate the secretion of saliva. Atropic poisoning leaves no characteristic post-mortem lesions.

**Tropeïns** — are ester-like derivatives of tropin with acids, similar to atropin. Many such have been formed with organic acids, benzoic, salicylic, etc. That formed with mandelic acid (p. 408) is known as **homatropin**, $C_8H_{14}N.OOC.CH(OH).C_6H_5$, and is used as a mydriatic having a less prolonged action than atropin. Only those tropeïns whose acid radicals contain an alcoholic hydroxyl have a mydriatic action.

**Cocaïn** — $C_{17}H_{21}NO_4$ — the most important of the alkaloids of *Erythroxylon coca*, is closely related, chemically, to atropin. It crystallizes in large four- or six-sided prisms; f. p. 98°; sparingly soluble in water, readily soluble in alcohol, ether or chloroform, somewhat bitter at first, but causing paralysis of the sense of taste afterwards; strongly alkaline. Its hydrochlorid, used as a local anæsthetic, crystallizes in prismatic needles, readily soluble in water. When boiled with water, cocaïn is hydrolised into **benzoyl-ecgonin**, $C_{16}H_{19}NO_4$, and methylic alcohol. If the saponification be effected by baryta, or by concentrated mineral acids, it is more complete, and **ecgonin**, $C_9H_{15}NO_3$, and benzoic acid and methylic alcohol are formed. Cocaïn may also be regenerated by acting upon ecgonin with a mixture of methyl iodid and benzoic anhydrid. Or, by substituting other alkyl iodids for that of methyl, other alkaloids, homologous with cocaïn, may be obtained. Ecgonin combines with bases to form salts, and also with anhydrids to form esters. It is, therefore, both acid and basic in character, and yields numerous products of derivation besides cocaïn. Cocaïn is the methyl ester of benzoyl-ecgonin, and ecgonin is tropin-$\beta$-carboxylic acid. Compare the formulæ of ecgonin and cocaïn below with those of tropin and atropin (p. 476):




Tropin-$\beta$-carboxylic acid.
Ecgonin.




Methyl-benzoyl ecgonate
Cocaïn.

ANALYTICAL CHARACTERS.—The reactions of cocaïn are not very marked. (1) Picric acid forms a yellow ppt. in concentrated solutions. (2) A solution of iodin in KI solution gives a fine red precipitate in a solution containing 1 to 10,000 of cocaïn. (3) When cocaïn or one of its salts, dried at 100° (212° F.), is moistened with fuming $HNO_3$, evaporated to dryness, and the residue taken up with alcoholic solution of KHO, a strong odor resembling that of peppermint is developed, due to the formation of ethyl benzoate.

Pilocarpin—$C_{11}H_{16}N_2O_2$—occurs in jaborandi, along with two other alkaloids, jaborin, $C_{22}H_{32}N_4O_4$(?), and pilocarpidin, $C_{10}H_{14}N_2O_2$, and an essential oil, consisting principally of pilocarpene, $C_{10}H_{16}$. It is colorless, crystalline, readily soluble in water, alcohol, ether and chloroform. It is converted by heat into jaborin; and by $HNO_3$ or HCl into a mixture of jaborin and jaborandin, $C_{10}H_{12}N_2O_2$. Like piperin, atropin, cocaïn, etc., it is ethereal in character and is decomposed into $CO_2$, methylamin, butyric acid, and pyridin bases by KHO or NaHO. When oxidized by potassium permanganate it yields pyridin-tartronic acid, $C_5H_4N.C(OH)(COOH)_2$, and this, on further oxidation, nicotinic acid, $C_5H_4N.COOH$. When its hydrochlorid is heated to 200°, in presence of $H_2O$, it takes up water and is decomposed into pilocarpidin and methylic alcohol. Conversely, pilocarpin is produced by the action of methyl iodid upon pilocarpidin. Although the constitution of pilocarpin is not established, the above and other reactions indicate that it contains the pyridin ring, to which the cyclic group, $C_6H_{12}NO_2$, is attached in the $\beta$ position; and that it is methyl-pilocarpidin.

Other alkaloids belonging to this group are: trigonellin, $C_7H_7NO_2$, from fenugreek; arecolin, $C_8H_{13}NO_2$, arecaïdin, $C_7H_{11}NO_2$, arecaïn, $C_7H_{11}NO_2$, and guvacin, $C_6H_9NO_2$, from the betel-nut; chrysanthemin, $C_{14}H_{28}N_2O_3$, from chrysanthemum; hyoscyamin, and pseudohyoscyamin, isomeric with atropin, and hyoscin, $C_{17}H_{23}NO_4$, from various species of *Solanaceæ;* pelletierin, $C_8H_{15}NO$, and its derivatives, from pomegranate-seeds; sparteïn, $C_{15}H_{26}N_2$, from broom; and cytisin, $C_{11}H_{14}N_2O$, from laburnum-seeds.

## QUINOLIN ALKALOIDS.

Cinchona Alkaloids—Although by no means so complex a substance as opium, cinchona bark contains a great number of substances: *quinin, cinchonin, quinidin, cinchonidin, aricin; quinic, quinotannic* and *quinovic acids; cinchona-red*, etc. Of these the most important are quinin and cinchonin.

Quinin—Quinina (U. S.)—$C_{20}H_{24}N_2O_2+n$ Aq—324+*n*18—exists in the bark of a variety of trees of the genera *Cinchona* and *China*,

which vary considerably in their richness in this alkaloid. The best samples of calisaya bark contain from 30 to 32 parts per 1,000 of the sulfate; the intermediate grades 4 to 20 parts per 1,000; inferior grades of bark contain from mere traces to 6 parts per 1,000.

It is known in three different states of hydration, with 1, 2, and 3 Aq, and anhydrous. The anhydrous form is an amorphous, resinous substance, obtained by evaporation of solutions in anhydrous alcohol or ether. The first hydrate is obtained in crystals by exposing to air recently precipitated and well-washed quinin. The second by precipitating by ammonia a solution of quinin sulfate, in which H has been previously liberated by the action of Zn upon $H_2SO_4$; it is a greenish, resinous body, which loses $H_2O$ at 150° (302° F.). The third, that to which the following remarks apply, is formed by precipitating solutions of quinin salts with ammonia.

It crystallizes in hexagonal prisms; very bitter; fuses at 57° (134.6° F.); loses 1 Aq at 100° (212° F.), and the remainder at 125° (257° F.); becomes colored, swells up, and, finally, burns with a smoky flame. It does not sublime. It dissolves in 2,200 pts. of cold water, in 763 of hot water, very soluble in alcohol and chloroform; soluble in amyl alcohol, benzene, fatty and essential oils, and ether. Its alcoholic solution is powerfully lævogyrous, $[a]_D$=—270.7° at 18° (64.4° F.), which is diminished by increase of temperature, but increased by the presence of acids.

ANALYTICAL CHARACTERS.—(1) Dilute $H_2SO_4$ dissolves quinin in colorless but fluorescent solution (see below). (2) Solutions of quinin salts turn green when treated with chlorin-water and then with ammonium hydroxid. (3) Chlorin passed through water holding quinin in suspension forms a red solution. (4) Solution of quinin treated with chlorin-water and then with fragments of potassium ferrocyanid becomes pink, passing to red.

SULFATE—*Disulfate*—**Quininæ sulfas** (U. S.)—**Quiniæ sulfas** (Br.)—$SO_4(C_{20}H_{25}N_2O_2)_2+7Aq$—746+126—crystallizes in prismatic needles; very light; intensely bitter; phosphorescent at 100° (212° F.); fuses readily; loses its Aq at 120° (248° F.), turns red, and finally carbonizes; effloresces in air, losing 6 Aq; soluble in 740 pts. of water at 13° (55.4° F), in 30 pts. of boiling water, and 60 pts. of alcohol. Its solution with alcoholic solution of iodin deposits brilliant green crystals of **iodoquinin sulfate.**

HYDROSULFATE—**Quininæ bisulfas** (U. S.)—$SO_4H(C_{20}H_{25}N_2O_2)+7$ Aq —422+126—is formed when the sulfate is dissolved in excess of dilute $H_2SO_4$. It crystallizes in long, silky needles, or in short, rectangular prisms; soluble in 10 pts. of water at 15° (59° F.). Its solutions exhibit a marked fluorescence, being colorless, but showing a

fine pale-blue color when illuminated by a bright light against a dark background.

By the action of alkaline hydroxids upon quinin, formic acid, quinolin (p. 468), and pyridin bases (p. 459) are produced.

Concentrated HCl at 140°–150° (284°–302° F.) decomposes quinin with separation of methyl chlorid and formation of apoquinin, $C_{19}H_{22}N_2O_2$, an amorphous base.

Oxidizing agents produce from quinin oxalic acid and pyridin carboxylic acids, notably pyridin-2, 3-dicarboxylic, or cinchomeronic, acid, $C_5H_3N(COOH)_2$, which are also formed by oxidation of cinchonin.

Although cinchonin differs from quinin in composition by $CH_2O$, and although the decompositions of the two bases show them both to be related to the quinolin and pyridin bases, attempts to convert cinchonin into quinin have resulted only in the formation of other products, among which is an isomere of quinin, oxycinchonin.

Methylquinin, $C_{20}H_{24}N_2O_2CH_3$, is a base which has a curare-like action.

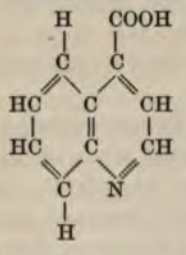
Cinchonin—Cinchonina (U. S.)—$C_{19}H_{22}N_2O$—294—occurs in Peruvian bark to the amount of from 2 to 30 pts. per 1,000. It crystallizes without Aq in colorless prisms; fuses at 150° (302° F.); soluble in 3,810 pts. of water at 10° (50° F.), in 2,500 pts. of boiling water; in 140 parts of alcohol, and in 40 pts. of chloroform. The salts of cinchonin resemble those of quinin in composition; are quite soluble in water and in alcohol; are not fluorescent; are permanent in air; and are phosphorescent at 100° (212° F.).

Quinidin and Quinicin—are bases isomeric with quinin; the former occurring in cinchona bark, and distinguishable from quinin by its strong dextrorotary power; the second a product of the action of heat on quinin, not existing in cinchona.

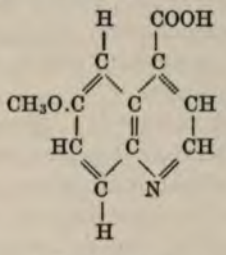
Cinchonidin—a base, isomeric with cinchonin, occurring in certain varieties of bark; lævogyrous. At 130° (266° F.), $H_2SO_4$ converts it into another isomere, cinchonicin.

Constitution of Cinchona Alkaloids—The constitution of no cinchona alkaloid has yet been completely determined. Enough has, however, been ascertained to show that cinchonin and quinin contain a quinolin nucleus, united to another cyclic nucleus, containing the second N atom, and which is probably a modified piperidin. The difference between the empirical formulæ of cinchonin, $C_{19}H_{22}N_2O$, and of quinin, $C_{20}H_{24}N_2O_2$, is $CH_2O$ in favor of the latter, which would represent the substitution of methoxyl, $CH_3O$, for H. When cinchonin and quinin are oxidized by chromic acid they yield two quinolin-carboxylic acids also differing from each other by $CH_2O$. Cinchonin yields cinchoninic acid, which is known to be γ-quinolin

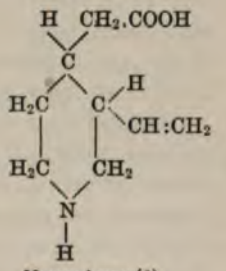
carboxylic acid; while quinin yields quinic acid, which has been shown to be the methyl-phenol ether of p-oxyquinolin-γ-carboxylic acid (see formulæ below). Therefore the group $CH_2O$, by which cinchonin and quinolin differ, exists in the quinolin ring, and the "second half," or the portion of the molecule other than the quinolin ring, is the same in the two alkaloids. This is further proven by the fact that on decomposition by $PCl_5$ and subsequent treatment with alcoholic KHO, cinchonin yields lepidin, $C_{10}H_9N$, the next superior homologue of quinolin, $C_9H_7N$, while quinin yields p-methoxy-lepidin, $C_{10}H_8(OCH_3)N$, and the other product of the decomposition is one and the same substance from either alkaloid, a substance which has been called **meroquinene**, $C_9H_{15}NO_2$, which on treatment with $HgCl_2$ and HCl is converted into β-ethyl-γ-methyl-pyridin, and whose probable constitution is expressed by the formula given below. So far as determined, therefore, the formulæ of cinchonin and of quinin are those here given, the arrangement of the group $C_{10}H_{15}(OH)N$ remaining to be determined :



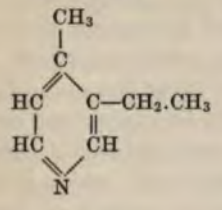
Cinchoninic acid, (γ-quinolin carboxylic acid).



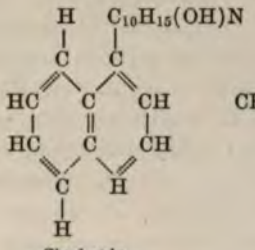
Quinic acid, (3-Methoxyquinolin-γ-carboxylic acid).



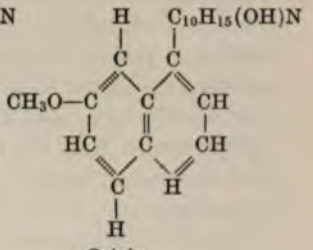
Meroquinene (?)



β-Ethyl-γ-methyl-pyridin.



Cinchonin.



Quinin.

**Alkaloids of the Loganiaceæ—Strychnos Alkaloids.**—This group includes strychnin and brucin and their alkyl derivatives, and the curare alkaloids.

**Strychnin**—$C_{21}H_{22}N_2O_2$—exists in the seeds and bark of different varieties of *Strychnos*, notably *Strychnos nux-vomica*.

It crystallizes on slow evaporation of its solutions in orthorhombic

prisms; very sparingly soluble in water and in strong alcohol; soluble in 5 parts of chloroform. Its aqueous solution is intensely bitter, the taste being perceptible in a solution containing 1 part in 200,000.

It is a powerful base; neutralizes and dissolves in concentrated $H_2SO_4$ without coloration, and precipitates many metallic oxids from solutions of their salts. Its salts are mostly crystallizable, soluble in water and in alcohol, and intensely bitter. The *acetate* is the most soluble. The *neutral sulfate* crystallizes, with 7 Aq, in rectangular prisms. Methyl and ethyl iodids react with strychnin to produce methyl or ethylstrychnium iodids, white, crystalline substances, producing an action on the economy similar to that of curare. Heated with fuming $HNO_3$, strychnin yields picric acid. Heated with baryta water to 130°, it yields isostrychnic acid, $C_{20}H_{22}N_2O.COOH$; and when treated with sodium alcoholate, strychnic acid, by addition of $H_2O$. By boiling with concentrated hydriodic acid and red phosphorus it is converted into desoxystrychnin, $C_{21}H_{22}N_2O$, which is further reduced by electrolysis to dihydrostrychnolin, $C_{21}H_{26}N_2$. Strychnin itself, by electrolysis, forms two bases, tetrahydro-strychnin, $C_{21}H_{26}N_2O_2$, and strychnidin, $C_{21}H_{24}N_2O$. But little is known of the constitution of strychnin, which is, however, probably a derivative of tetrahydroquinolin.

ANALYTICAL CHARACTERS.—(1) Dissolves in concentrated $H_2SO_4$, without color. The solution deposits strychnin when diluted with water, or when neutralized with magnesia or an alkali. (2) If a fragment of potassium dichromate (or other substance capable of yielding nascent oxygen) be drawn through a solution of strychnin in $H_2SO_4$, it is followed by a streak of color; at first blue (very transitory and frequently not observed), then a brilliant violet, which slowly passes to rose-pink, and finally to yellow. Reacts with $\frac{1}{50000}$ grain of strychnin. (3) A dilute solution of potassium dichromate forms a yellow, crystalline ppt. in strychnin solutions, which, when washed and treated with concentrated $H_2SO_4$, gives the play of colors indicated in 2. (4) If a solution of strychnin be evaporated on a bit of platinum foil, the residue moistened with concentrated $H_2SO_4$, the foil connected with the + pole of a single Grove cell, and a platinum wire from the — pole brought in contact with the surface of the acid, a violet color appears upon the surface of the foil. (5) Strychnin and its salts are intensely bitter. (6) A solution of strychnin introduced under the skin of the back of a frog causes difficulty of respiration and tetanic spasms, which are aggravated by the slightest irritation, and twitching of the muscles during the intervals between the convulsions. With a small frog, $\frac{1}{60000}$ grain of strychnium acetate will produce tetanic spasms in ten minutes. White mice, 14 to 16 days old, are even more susceptible to the action of strychnin than

frogs. (7) Solid strychnin, moistened with a solution of iodic acid in $H_2SO_4$, produces a yellow color, changing to brick-red, and then to violet-red. (8) Moderately concentrated $HNO_3$ colors strychnin yellow in the cold. (9) A warm solution of strychnin in dilute $HNO_3$ produces a scarlet-red color on addition of a little $KClO_3$. A drop or two of ammonia changes this to brown. On evaporation to dryness, a green residue remains, which forms a green solution in water, changes to orange-brown with KHO, and returns to green with $HNO_3$.

TOXICOLOGY.— Strychnin produces a sense of suffocation, thirst, tetanic spasms, usually opisthotonos, sometimes emprosthotonos, occasionally vomiting, contraction of the pupils during the spasms, and death, either by asphyxia during a paroxysm, or by exhaustion during a remission. The symptoms appear in from a few minutes to an hour after taking the poison, usually in less than twenty minutes; and death in from five minutes to six hours, usually within two hours. Death has been caused by ¼ grain, and recovery has followed the taking of 20 grains.

The treatment should consist in bringing the patient under the influence of chloral hydrate or of chloroform, and then washing out the stomach. The patient should be kept as quiet as possible, as the slightest unexpected irritation will produce a spasm.

Strychnin is one of the most stable of the alkaloids, and may remain for a long time in contact with putrefying organic matter without suffering decomposition.

**Brucin** — $C_{23}H_{26}N_2O_4 + 4Aq — 394 + 72$ — accompanies strychnin. It forms oblique rhomboidal prisms, which lose their Aq in dry air. Sparingly soluble in $H_2O$, readily soluble in alcohol, chloroform, and amyl alcohol; intensely bitter. It is a powerful base and most of its salts are soluble and crystalline. Its action on the economy is similar to that of strychnin, but much less energetic.

ANALYTICAL CHARACTERS. — (1) Concentrated $HNO_3$ colors it bright red, soon passing to yellow; stannous chlorid, or colorless $NH_4HS$, changes the red color to violet. (2) Chlorin-water, or Cl, colors brucin bright red, changed to yellowish-brown by $NH_4HO$.

**Curarin** — $C_{36}H_{35}N(?)$ — is an alkaloid obtainable from the South American arrow-poison, *curare*, or *woorara*. It crystallizes in four-sided, colorless prisms, which are hygroscopic, faintly alkaline, and intensely bitter.

Curarin dissolves in $H_2SO_4$, forming a pale-violet solution, which slowly changes to red. If a crystal of potassium dichromate be drawn through the $H_2SO_4$ solution, it is followed by a violet coloration, which differs from the similar color obtained with strychnin under similar circumstances, in being more permanent, and in the absence of the following pink and yellow tints.

## ISOQUINOLIN ALKALOIDS.

The opium, hydrastis, berberis and corydalis alkaloids are included in this group. Of the opium alkaloids, papaverin, narcotin and narceïn are certainly derivatives of isoquinolin. Morphin and codeïn, on the other hand, do not contain the isoquinolin nucleus, but a phenanthrene nucleus having a nitrogen-containing ring condensed upon it. But until the constitution of these two alkaloids is established with more completeness it is not desirable to separate them from their congeners (see p. 488).

**Opium Alkaloids.**— Opium is the dried juice obtained by making incisions in the unripe capsules of the poppy, *Papaver somniferum*. It is of exceeding complex composition, and contains meconic (p. 459), lactic and sulfuric acids, with which the alkaloids are in combination, meconin (p. 407), gum, caoutchouc, wax, sugar, resins, etc., and a number of alkaloids. Some twenty alkaloids have been obtained from opium, but of these several are probably produced by the processes of extraction. The most important of the natural alkaloids and the average percentage in which they exist in opium of good quality are: morphin, 10%; narcotin, 6%; papaverin, 1%; codeïn, 0.3%; narceïn, 0.2%; and thebaïn, 0.15%.

**Morphin — Morphina (U. S.)** — $C_{17}H_{19}NO_3 + Aq$ — 285 + 18 — crystallizes in colorless prisms; odorless, but very bitter; it fuses at 120° (248° F.), losing its Aq. More strongly heated, it swells up, becomes carbonized, and finally burns. It is soluble in 1,000 pts. of cold water, in 400 pts. of boiling water; in 265 pts. of alcohol of 90 per cent. at 10°, and in 33 pts. of boiling alcohol of the same strength; in 373 pts. of cold amyl alcohol, much more soluble in the same liquid warm; almost insoluble in aqueous ether; rather more soluble in alcoholic ether; almost insoluble in benzene; soluble in 2,500 pts. of chloroform at 9°, and in 45 pts. at 56°. All the solvents dissolve morphin more readily and more copiously when it is freshly precipitated from solutions of its salts than when it has assumed the crystalline form.

Morphin combines with acids to form crystallizable salts, of which the hydrochlorid, sulfate and acetate are used in medicine. If morphin be heated for some hours with excess of HCl, under pressure, to 150° (302° F.), it loses water, and is converted into a new base— apomorphin, $C_{17}H_{17}NO_2$.

By heating together acetic anhydrid and morphin, three modifications, $\alpha$, $\beta$, $\gamma$, of acetyl-morphin, $C_{17}H_{18}(C_2H_3O)NO_3$, are formed. Similarly substituted butyryl-, benzoyl-, succinyl-, camphoryl-, methyl-, and ethyl-morphin are also known.

Morphin is readily oxidized and is a strong reducing agent. It

reduces the salts of gold and silver in the cold. It is oxidized by atmospheric oxygen when it is in alkaline solution, as well as by nitrous acid, potassium permanganate, potassium ferricyanid, or ammoniacal cupric sulfate, with the formation of a non-toxic compound which has received the names **oxymorphin, oxydimorphin, dehydromorphin,** and **pseudomorphin** $(C_{17}H_{18}NO_3)_2$, whose molecule consists of two morphin molecules, united with loss of $H_2$, and which is an inferior degree of condensation to **trimorphin** and **tetramorphin**, two amorphous, basic products of the action of $H_2SO_4$ on morphin at 100° (212° F.). When morphin is distilled with powdered zinc, the principal product of the reaction is phenanthrene, accompanied by ammonia, trimethylamin, pyrrole, pyridin, and a product having the formula $C_{17}H_{11}N$, probably phenanthrene-quinolin.

The salts of morphium are crystalline. The *acetate* is a white crystalline powder, soluble in 12 parts of water, which decomposes on exposure to air, with loss of acetic acid. The *chlorid* is less soluble, but more permanent than the acetate. The *sulfate* is the form in which morphin is the most frequently used in medicine. It is a very light, crystalline, feathery powder; odorless, bitter, and neutral in reaction. It dissolves in 24 parts of water. Its solutions deposit morphin as a white precipitate on addition of an alkali. The crystals contain 5 Aq, which they lose at 130° (266 F.).

ANALYTICAL CHARACTERS.—(1) It is colored orange, changing to yellow, by $HNO_3$. (2) A neutral solution of a morphium salt gives a blue color with neutral solution of ferric chlorid. (3) A solution of molybdic acid in $H_2SO_4$ (Fröhde's reagent) gives with morphin a violet color, changing to blue, dirty green, and faint pink. Water discharges the color. (4) Take two test-tubes. Into one (*a*) put the solution of morphin, into the other (*b*) an equal bulk of $H_2O$. Add to each a granule of iodic acid and agitate; *a* becomes yellow or brown, *b* remains colorless. To each add a small drop of chloroform and agitate: the $CHCl_3$ in *a* is colored violet, that in *b* remains colorless. Float some very dilute ammonium hydroxid solution on the surface of the liquid in *a;* a brown band is formed at the junction of the layers. (5) Moisten the solid material with HCl to which a small quantity of $H_2SO_4$ has been added, and heat in an air oven at 110° until HCl is expelled: a violet-colored liquid residue remains. Add to this a drop or two of water containing a little HCl, and neutralize with powdered sodium bicarbonate in slight excess: a pink or rose color is produced, most distinctly visible on the bubbles. Add a drop of water and a drop or two of alcoholic solution of iodin: a green color is developed. This reaction, known as the Pellagri test, is based upon the conversion of morphin into apomorphin, and consequently reacts with that alkaloid.

(6) Moisten the solid with concentrated $H_2SO_4$, and heat cautiously until white fumes begin to be given off, cool and touch the liquid with a glass rod moistened with dilute $HNO_3$: a fine blue-violet color, changing to red and then to orange. If the $H_2SO_4$ contains oxids of nitrogen, as it usually does, a violet tinge will be produced before addition of $HNO_3$, but then becomes much more intense. This reaction, known as the Husemann, may be applied by allowing the solid to remain in contact with $H_2SO_4$ for fifteen to eighteen hours in place of heating.

These are the most important tests for morphin, and affirmative results with all of them prove the presence of that alkaloid. Other tests have been suggested, among which are the following: (7) Solution of morphium acetate produces a gray ppt. when warmed with ammoniacal silver nitrate solution; and the filtrate turns red or pink with $HNO_3$. (8) Auric chlorid gives a yellow ppt., turning violet-blue, with solutions of morphium salts. (9) Add solution of $Fe_2Cl_6$ (2-16) to solution of potassium ferricyanid (the mixture must not assume a blue color), add morphin: a deep-blue color. (10) Heat morphin with concentrated $H_2SO_4$ to 200° (392° F.) until green-black; add a drop of the liquid cautiously to water: the solution turns blue. Shake a portion with ether: the ether turns purple. Shake another portion with chloroform: the chloroform turns blue. (11) Warm the solid alkaloid with concentrated $H_2SO_4$; add cautiously a few drops of alcoholic solution of KHO (30%): a yellow color, changing to dirty-red, then steel-blue, and sky-blue, and, with a further quantity of KHO solution, cherry-red. (12) A mixture of morphin and cane-sugar (1 to 4) added to concentrated $H_2SO_4$ gives a dark-red color, which is intensified by a drop of bromin-water.

Codeïn—Codeina (U. S.)—$C_{18}H_{21}NO_3+Aq$—299+18—crystallizes in large rhombic prisms, or from ether, without Aq, in octahedra; bitter; soluble in 80 pts. cold water; 17 pts. boiling water; very soluble in alcohol, ether, chloroform, benzene; almost insoluble in petroleum-ether.

Codeïn is the methyl ether of morphin, or its superior homologue, and resembles that alkaloid in some of its reactions; thus under similar circumstances both form apomorphin; and morphin may be converted into codeïn by the action of methyl iodid in the presence of KHO. Codeïn, however, only contains one OH group, and forms a monoacetyl derivative with acetyl chlorid, while morphin produces a diacetyl compound.

Analytical Characters.—(1) Cold concentrated $H_2SO_4$ forms with it a colorless solution, which turns blue after some days, or when warmed. (2) Fröhde's reagent dissolves it with a dirty-green color, which after a time turns blue. (3) Chlorin-water forms with it a colorless solution, which turns yellowish-red with $NH_4HO$.

**Narceïn** — $C_{23}H_{27}NO_8+2Aq$—463+36—crystallizes in bitter, prismatic needles; sparingly soluble in water, alcohol, and amyl alcohol; insoluble in ether, benzene, and petroleum-ether.

ANALYTICAL CHARACTERS.—(1) Concentrated $H_2SO_4$ dissolves it with a gray-brown color, which changes to red, slowly at ordinary temperatures, rapidly when heated. (2) Fröhde's reagent colors it dark olive-green, passing to red after a time, or when heated. (3) Iodin solution colors it blue-violet, like starch.

**Narcotin** — $C_{22}H_{23}NO_7$— 413 — crystallizes in transparent prisms, almost insoluble in water and in petroleum-ether; soluble in alcohol, ether, benzene, and chloroform. Its salts are mostly uncrystallizable, unstable, and readily soluble in water and in alcohol.

Narcotin is decomposed by $H_2O$ at 140° (284° F.), by dilute $H_2SO_4$, or by baryta, with formation of **opianic acid**, $C_{10}H_{10}O_5$, and **hydrocotarnin**, $C_{12}H_{15}NO_3$. Reducing agents decompose it into hydrocotarnin and **meconin**, $C_{10}H_{10}O_4$. Oxidizing agents convert it into opianic acid and **cotarnin**, $C_{12}H_{13}NO_3$.

ANALYTICAL CHARACTERS.—(1) Concentrated $H_2SO_4$ forms with it a solution, at first colorless, in a few moments yellow, and after a day or two red. (2) Its solution in dilute $H_2SO_4$, if gradually evaporated until the acid volatilizes, turns orange-red, bluish-violet and reddish-violet. (3) Fröhde's reagent dissolves it with a greenish color, passing to cherry-red.

**Papaverin** — $C_{20}H_{21}NO_4$ — crystallizes in prisms; almost insoluble in water, easily soluble in chloroform and in hot alcohol. It is optically inactive. It forms a colorless solution with concentrated $H_2SO_4$, which turns dark-violet when heated. Acetic anhydrid has no action upon it.

**Thebaïn — Paramorphin** — $C_{19}H_{21}NO_3$—311—crystallizes in white plates; tasteless when pure; insoluble in water, soluble in alcohol, ether and benzene.

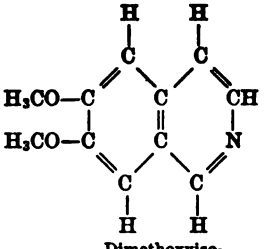
ANALYTICAL CHARACTERS.—(1) With concentrated $H_2SO_4$: an immediate bright-red color, turning to yellowish-red. (2) Its solution in chlorin-water turns reddish-brown with $NH_4HO$. (3) With Fröhde's reagent: same as 1.

**Apomorphin** — $C_{17}H_{17}NO_2$ — is used hypodermically as an emetic in the shape of the chlorid. It is obtained by sealing morphin, with an excess of strong HCl, in a thick glass tube, and heating the whole to 140° (252° F.) for two to three hours. It is obtained also by the same process from codeïn. The free alkaloid is a white, amorphous solid, difficultly soluble in water. The chlorid forms colorless, shining crystals, which have a tendency to assume a greenish tint on exposure to light and air. It is odorless, bitter and neutral; soluble in 6.8 parts of cold water.

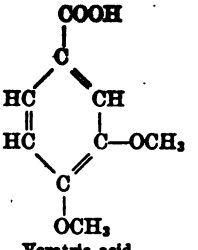
**Relations and Constitution of the Opium Alkaloids.**—The alkaloids of opium may be arranged in two groups: (I) Including those which are strong bases, are highly poisonous, and contain three or four atoms of oxygen; (II) those which are weak bases and contain four to nine oxygen atoms. So far as known, the alkaloids of the first group contain the phenanthrene-pyridin nucleus, while those of the second group are derivatives of isoquinolin. The six principal alkaloids above mentioned are equally divided between the two groups:

| I. | | II. | |
|---|---|---|---|
| Morphin | $C_{17}H_{19}NO_3$ | Papaverin | $C_{20}H_{21}NO_4$ |
| Codein | $C_{18}H_{21}NO_3$ | Narcotin | $C_{22}H_{23}NO_7$ |
| Thebain | $C_{19}H_{21}NO_3$ | Narcein | $C_{23}H_{27}NO_8$ |

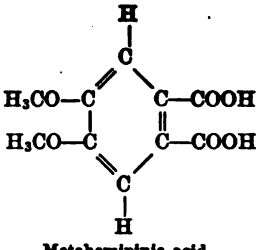
**Papaverin** was first recognized as an isoquinolin derivative. On oxidation of papaverin by potassium permanganate, **papaveraldin**, $C_{20}H_{19}NO_5$, is formed. This, on fusion with caustic potash, yields veratric acid, which is 3, 4-dimethoxy-benzoic acid, $C_6H_3.COOH:(OCH_3)_{(3,4)}$, and dimethoxyisoquinolin, the constitution of the latter being established by its further decomposition into metahemipinic acid and $\alpha$-$\beta$-$\gamma$-pyridin-tricarboxylic acid. The relations of papaverin and its products of decomposition are shown by the following formulæ:



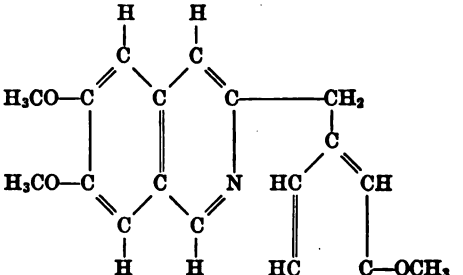
Dimethoxyisoquinolin.



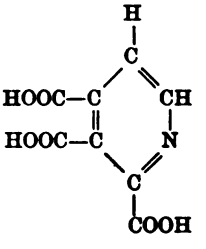
Veratric acid, (3, 4-Dimethoxy-benzoic acid).



Metahemipinic acid, (4, 5-Dimethoxy-o-phthalic acid).



Papaverin, (Tetramethoxy-benzyl-α-isoquinolin).

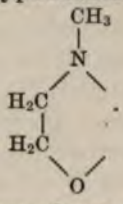


α-β-γ-Pyridin-tricarboxylic acid.

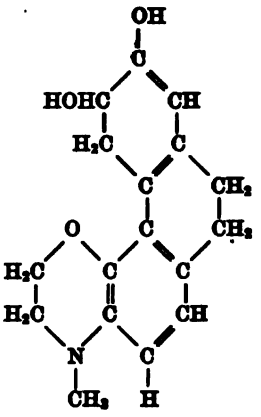
**Narcotin,** $C_{22}H_{23}NO_7$, is converted by oxidation into opianic acid, $C_{10}H_{10}O_5$ (p. 408), and **cotarnin,** $C_{12}H_{15}NO_4$. By hydrolysis it yields opianic acid and **hydrocotarnin,** $C_{12}H_{15}NO_3$; and by reduction, meconin, $C_{10}H_{10}O_4$ (p. 407), and hydrocotarnin. Narcotin, therefore, contains the nuclei of opianic acid, or of meconin, and of hydrocotarnin. The constitution of opianic acid is known, as well as that of its reduction product, meconin, but that of hydrocotarnin is not completely established. It is, however, a derivative of isoquinolin, containing one of the three methoxy groups ($CH_3O$) which exist in narcotin, and a bivalent group $-O.CH_2.O-$ attached to the benzene ring; and a methyl group, united to the N atom in the pyridin ring.

**Narceïn,** $C_{23}H_{27}NO_8$, is formed by the action of caustic potash upon narcotin iodmethylate: $C_{22}H_{23}NO_7.CH_3I+KHO=KI+C_{23}H_{27}NO_8$.

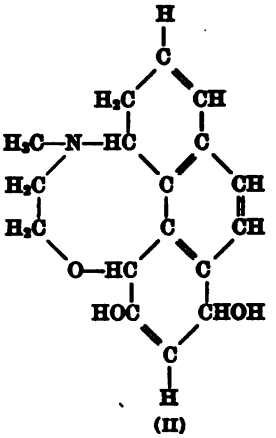
**Morphin,** $C_{17}H_{19}NO_3$, and **codeïn,** $C_{18}H_{21}NO_3$, are closely related. Codeïn is produced by the action of methyl iodid upon morphin-potassium: $C_{17}H_{18}KNO_3+CH_3I=KI+C_{17}H_{18}(CH_3)NO_3$. It is, therefore, **methyl-morphin.** By the further action of methyl iodid upon codeïn in alcoholic solution, **codeïn methyl iodid,** $C_{18}H_{21}NO_3:CH_3I$, is produced, and this, when warmed with KHO, is converted into **methyl-morphin methine,** $C_{17}H_{19}NO_3:CH.CH_3$. The last-named substance is decomposed by acetic anhydrid into methyldioxyphenanthrene and oxethyl-dimethyl-amin: $C_{17}H_{19}NO_3:CH.CH_3=C_{14}H_8\begin{matrix}OH\\O.CH_3\end{matrix}+N\begin{matrix}CH_3\\CH_3\\CH_2.CH_2.OH\end{matrix}$; and other morphin and codeïn derivatives are similarly decomposed, with formation, on the one hand, of a non-nitrogenized oxy-phenanthrene compound, and, on the other, an oxyamin or a trialkyl-amin. Upon these facts, it is concluded, that the morphin and codeïn molecules consist of an oxyphenanthrene group,



upon which is fused a nitrogenized group, . It is also recognized that the two hydroxyls are in the same phenanthrene ring, and that one of them is phenolic, the other alcoholic; also that one methyl group is attached to the nitrogen atom. The disposal of the hydrogen and hydroxyls in the phenanthrene nucleus and the position of attachment of the nitrogenized group above referred to remain undetermined. Two formulæ of constitution of morphin have been proposed, either of which is in consonance with the facts at present known:



(I)



(II)

**The formula of codeïn is derived from either formula by substitution of $CH_3$ for H in the phenolic OH; that of apomorphin by removal of $H_2O$.**

**Thebaïn, $C_{19}H_{21}NO_3$, is decomposed by acetic anhydrid in a manner quite analogous to the decomposition of morphin, above referred to, but yielding a dimethoxy-phenolic derivative of phenanthrene, called thebaol, and methyl-oxethyl-amin: $C_{19}H_{21}NO_3+H_2O=(CH_3O)_2C_{14}H_7.OH+N\overset{H}{\underset{CH_2.CH_2.OH}{-CH_3}}$.** Like morphin and codeïn, it is therefore a phenanthrene-pyridin derivative.

**Toxicology of Opium and its Derivatives.**— Opium, its preparations and the alkaloids obtained from it are all active poisons. The alkaloids have not all the same action. In soporific effects, beginning with the most powerful, they rank thus: narcotin, morphin, codeïn; in tetanizing action: thebaïn, papaverin, narcotin, codeïn, morphin; in toxic action: thebaïn, codeïn, papaverin, narceïn, morphin, narcotin.

The symptoms set in in from ten minutes to three hours, exceptionally "immediately," or only after eighteen hours. They are divisible into three periods: (1) a stage of excitement, marked by great physical activity, loquacity and imaginative power; is of short duration; longest in opium habitues, absent with large doses; (2) a period of sopor, in which there are diminished sensibility, weariness, contracted pupils, pale face, livid lips, drowsiness, increasing to deep sleep, from which, however, the patient may be roused, and when so roused is coherent in speech. This stage merges insensibly into the third, that of coma. The patient can no longer be aroused, even by violent means. The face is pale, the lips cyanosed, the muscular system completely relaxed, the reflexes abolished, the pupils contracted greatly, and insensible to light, the pulse slow, irregular,

compressible, and finally imperceptible, the respiration more and more infrequent, stertorous, shallow, and accompanied by mucous râles. Retention of urine begins early in the poisoning. The usual duration of a fatal poisoning is from six to twenty-four hours. Deaths have occurred in forty-five minutes and in three days.

The minimum lethal dose for a non-habituated adult is probably 3 to 4 grains. Young children are very susceptible. Tolerance to a remarkable degree is established by habit, both in children and in adults, and instances are reported in which 50 to 60 grains have been taken daily, without toxic effects, by morphin-takers.

The treatment should consist in washing out the stomach with a dilute solution of potassium permanganate, leaving about 500 cc. in the stomach, and in maintaining the respiration. In the first or second stage the "ambulatory treatment" should be adopted to prevent, if possible, the establishment of the third stage. If this stage develop, the main reliance is to be placed in maintaining the respiration by artificial methods, until the poison has been eliminated. Strong coffee, or caffeïn, by the mouth or rectum are of benefit. The same cannot be said of the atropin. The urine should be drawn by the catheter.

The opiates leave no post-mortem lesions, except such as are usually observed after death from asphyxia, i. e., congestion of the vessels of the brain and meninges, and of the lungs, and a dark, fluid condition of the blood.

## ALKALOIDS OF UNKNOWN CONSTITUTION.

Of the numerous alkaloids whose constitution is insufficiently known to permit of their classification, only a few can be here briefly considered :

**Alkaloids of the Aconites.**—The different species of *Aconitum* contain probably a number of alkaloids, but our knowledge of them is as yet extremely imperfect. The substances described as *aconitin*, *lycoctonin*, *napellin* are impure. It appears, however, that the principal alkaloids of *Aconitum napellus* and of *A. ferox*, although differing from each other, are both compounds formed by the union of **aconin**, $C_{26}H_{41}NO_{11}$, with the radical of benzoic acid in the former, and with that of veratric acid in the latter.

**Aconitin — Acetylbenzoyl-aconin** — $C_{26}H_{39}(CH_3.CO)(C_6H_5.CO)NO_{11}$ — the principal alkaloid of *A. napellus*, is a crystalline solid, almost insoluble in water, and very bitter. It is decomposed by $H_2O$ at 140° (284° F.) and by KHO into aconin and acetic and benzoic acids. It is very poisonous.

**Pseudo-aconitin**—$C_{36}H_{49}NO_{12}$—occurs in *A. ferox*. It is a crystalline solid, having a burning taste, and is extremely poisonous. On

decomposition by $H_2O$ at 140° (284° F.) it yields aconin and veratric acid.

**Japaconitin**—$C_{66}H_{88}N_2O_{21}$—has been obtained from the root of *A. japanicum*, and is a crystalline solid which is decomposed by alkalies into benzoic acid and **japaconin**, $C_{26}H_{41}NO_{10}$.

The color reactions described as characteristic of "aconitine" are not due to the alkaloid.

TOXICOLOGY.—Aconite and "aconitine" have been the agents used in quite a number of homicidal poisonings.

The symptoms usually manifest themselves within a few minutes; sometimes are delayed for an hour. There is numbness and tingling, first of the mouth and fauces, later becoming general. There is a sense of dryness and of constriction in the throat. Persistent vomiting usually occurs, but is absent in some cases. There is diminished sensibility, with numbness, great muscular feebleness, giddiness, loss of speech, irregularity and failure of the heart's action. Death may result from shock if a large dose of the alkaloid be taken, but more usually it is by syncope.

The treatment should be directed to the removal of unabsorbed poison by the stomach-pump, and washing out of the stomach with infusion of tea holding powdered charcoal in suspension. Stimulants should be freely administered.

**Alkaloids from other Sources.**—**Ergotin**—$C_{50}H_{52}N_2O_3$—and **Ecbolin** are two brown, amorphous, faintly bitter, and alkaline alkaloids obtained from ergot. They are readily soluble in water and form amorphous salts. The medicinal preparations known as ergotin are not the pure alkaloid.

**Colchicin**—$C_{17}H_{19}NO_5$—occurs in all portions of *Colchicum autumnale* and other members of the same genus. It is a yellowish-white, gummy, amorphous substance, having a faintly aromatic odor and a persistently bitter taste. It is slowly but completely soluble in water, forming faintly acid solutions. It forms salts which are, however, very unstable.

Concentrated $HNO_3$, or, preferably, a mixture of $H_2SO_4$, and $NaNO_3$, colors colchicin blue-violet. If the solution be then diluted with $H_2O$, it becomes yellow, and on addition of NaHO solution, brick-red.

**Veratrin**—**Veratrina**, U. S.—$C_{32}H_{52}N_2O_8$—occurs in *Veratrum officinalis* = *Asagræa officinalis*, accompanied by **Sabadillin**—$C_{20}H_{26}N_2O_5$—**Jervin**—$C_{30}H_{46}N_2O_3$—and other alkaloids. The substance to which the name **Veratrina**, U. S., applies is not the pure alkaloid, but a mixture of those occurring in the plant.

Concentrated $H_2SO_4$ dissolves veratrin, forming a yellow solution, turning orange in a few moments, and then, in about half an hour,

bright carmine-red. Concentrated HCl forms a colorless solution with veratrin, which turns dark-red when cautiously heated.

**Physostigmin — Eserin** — $C_{15}H_{21}N_3O_2$ — is an alkaloid existing in the Calabar bean, *Physostigma venenosum*. It is a colorless, amorphous solid, odorless and tasteless, alkaline and difficultly soluble in water. It neutralizes acids completely, with formation of tasteless salts. Its salicylate—**Physostigminæ salicylas, U. S.**—forms short, colorless, prismatic crystals, sparingly soluble in water.

Concentrated $H_2SO_4$ forms a yellow solution with physostigmin or its salts, which soon turns olive-green. Concentrated $HNO_3$ forms with it a yellow solution. If a solution of the alkaloid in $H_2SO_4$ be neutralized with $NH_4HO$, and the mixture warmed, it is gradually colored red, reddish-yellow, green, and blue.

**Emetin** — $C_{28}H_{40}N_2O_5$ — an alkaloid existing in *ipecacuanha* which crystallizes in colorless needles or tabular crystals, slightly bitter and acrid; odorless, and sparingly soluble in water.

It dissolves in concentrated $H_2SO_4$, forming a green solution, which gradually changes to yellow. With Fröhde's reagent it gives a red color, which soon changes to yellowish-green and then to green.

## PTOMAÏNS, LEUCOMAÏNS, TOXINS AND ANTITOXINS.

The name *ptomaïn*, derived from πτῶμα ("that which has fallen," i. e., a corpse), was first suggested by Selmi in 1878 to apply to a substance, or class of substances, first distinctly recognized, although not isolated, by him, which are produced from proteins during putrefaction, and which are alkaloids in the broader sense of that term. In the more restricted sense in which the term "alkaloid" is now used (p. 470), many of the best known ptomaïns are not true alkaloids, but amins, betaïns, oxyamins or diamins (pp. 328–334, 422). On the other hand, many ptomaïns are true alkaloids. Several of the superior homologues of pyridin (p. 460) are putrid products. A base, $C_8H_{11}N$, isomeric with collidin, formed during putrefaction of jelly-fish, on oxidation yields nicotinic acid, $C_5H_4N(COOH)$, which is also similarly produced from nicotin (p. 474), and also forms a chloroplatinate and an iodomethylate which have the characteristic properties of the like compounds produced from the pyridin bases (p. 459) and vegetable alkaloids. Other basic substances obtained from brown cod-liver oil, and probably formed by a modified putrefaction, are hydropyridin derivatives (p. 461). Among these are a dihydrolutidin, $C_7H_{11}N$, a dihydrocollidin, $C_8H_{13}N$, and a complex hydropyridic oxyacid, called **morrhuic acid**, $C_5H_5N\begin{smallmatrix}\diagup OH\\ \diagdown C_3H_6.COOH\end{smallmatrix}$. In-

dole and skatole, products of putrefaction, also come within the definition of the alkaloids.

The term "ptomaïn," as at present used, therefore, applies to substances of several different chemical classes, in some of which the nitrogen forms a part of a heterocyclic chain, while in others it is in a lateral chain of a carbocyclic compound, and in still others in an aliphatic molecule. **A ptomaïn may be defined as a basic compound, containing nitrogen, produced from protein material by the bacteria which cause putrefaction.** The use of the name in referring to similar compounds produced by other processes, or by other bacteria, is improper (see below).

Some ptomaïns are strongly alkaline and basic, others only feebly so. Some are liquid, oily and volatile, others fixed and crystalline. Some are actively poisonous, others practically inert. Some, notably those formed in the earlier stages of putrefaction, contain oxygen, others are made up of carbon, hydrogen and nitrogen. Some are very prone to oxidation, others are quite stable.

Several methods have been devised for the more or less complete separation of the ptomaïns, notably from vegetable alkaloids, none of which, however, can be relied upon to accomplish the object completely in all cases. Breiger's and Gautier's methods, for which the student is referred to special treatises, are the most elaborate. Partial separation can be effected by taking advantage of the fact that the oxalates of most of the ptomaïns are soluble in ether, in which the oxalates of most of the vegetable alkaloids are insoluble. Or those ptomaïns which are diamins can be separated by the benzoyl-chlorid method. In dilute, alkaline, aqueous solution the diamins form crystalline, insoluble dibenzoyl compounds when shaken with benzoyl chlorid. This is purified by solution in alcohol and re-precipitation by dilution with water (Udránsky and Baumann).

No general reaction is known capable of distinguishing the ptomaïns from other substances, nor is one to be expected, in view of the variation in their chemical constitution above referred to. Many of the ptomaïns are reducing agents, and consequently give a blue color with a mixture of ferric chlorid and potassium ferricyanid solutions (Brouardel and Boutmy's reaction); but all ptomaïns do not reduce, and some vegetable alkaloids, as morphin and veratrin, do.

It was feared that, as alkaloidal substances in many respects resembling those of vegetable origin are produced in the animal body, not only after death but during life, grave doubts would be cast upon the results of analyses made to detect the presence of poisonous vegetable alkaloids in the cadaver in cases of suspected poisoning. Such fears were by no means groundless, as there is abundant evidence that ptomaïns have been mistaken for vegetable

alkaloids in chemico-legal analyses. The ptomaïns, however, as well as the vegetable alkaloids, may be positively identified by a careful analysis, based upon the use, not of a single reaction, but of *all known reactions* for the alkaloid in question. Therefore, it is possible to positively predicate the existence or non-existence of a given vegetable alkaloid in a cadaver, but it can only be done after a thorough and conscientious examination by all physiological and chemical reactions.

The term "**toxin**" was first used by Brieger, and applied to such of the ptomaïns as are poisonous. It is now, however, better applied to basic substances similar chemically to the ptomaïns, but produced by pathogenic bacteria, either in living bodies or in appropriate culture media.

An alkaloid, many of whose chemical reactions have been determined, although its composition is unknown, has been obtained from the internal organs and dejecta of cholera victims, as well as from cultures of the comma bacillus. This alkaloid, when administered to animals, causes symptoms of poisoning and death.

From the cultures of the Koch-Eberth typhus bacillus an alkaloid has been isolated—**Typhotoxin**, $C_7H_{17}NO_2$—which, when administered to animals, causes paralysis, copious diarrhœa, and death.

**Tetanin**—$C_{13}H_{30}N_2O_4$—is an alkaloid obtained from cultures of a bacillus originating from a wound which had been the cause of death by tetanus. It forms a deliquescent chlorid, and a very soluble chloroplatinate. The free base or its chlorid, when injected into mice or guinea-pigs, causes clonic or tonic convulsions of the greatest intensity, which terminate in death.

**Mytilitoxin**—$C_6H_{15}NO_2$—is an alkaloid obtained from poisonous mussels, which, when administered to animals in small amount, causes the same symptoms as are produced by the mussels.

Another class of poisons, some of vegetable and others of animal origin, have the properties of proteins, and appear to belong to the classes of globulins, albumoses or peptones (p. 497). These are known as **toxalbumins**, and among them are included **abrin**, from jequirity (*Abrus precatorius*), **ricin**, from the castor-oil bean (*Ricinus communis*), **phallin**, from various toadstools (*Amanita*); the toxic constituents of the poisonous secretions of serpents, spiders, and insects; and the poisons produced by certain pathogenic bacteria, as those of diphtheria and cholera.

Other globulins are met with in the blood of animals, which neutralize the action of the toxalbumins, and which are more abundant in those individuals which have been rendered immune to the action of the particular toxalbumin whose action they modify. These are known as **antitoxins.**

**Leucomaïns** (from λευκόν = white of egg, because of their origin from albumin) are nitrogenous, basic substances which are produced in the bodies of animals during life as results of normal chemical processes. They are excreted in health, and if retained exert deleterious actions, more or less intense. The xanthin, or purin, bases (p. 356) and those of the creatin group (p. 335) are leucomaïns, and others occur in the urine.

Poisonings are exogenous or endogenous (p. 85). In exogenous poisonings the toxic agent, whether it be mineral, vegetable, animal, or synthetic, is introduced into the body from without. In the popular acceptation of the term all poisonings are exogenous. In endogenous poisonings the toxic agent, always organic, either a toxin, a toxalbumin or a leucomaïn, is produced in the body of the person affected. Endogenous poisonings are called diseases.

# SUBSTANCES OF UNKNOWN CONSTITUTION.

## PROTEINS—ALBUMINOUS COMPOUNDS.

The substances of this class are never absent from living animal and vegetable cells, to whose "life" they are indispensable. They are frequently referred to as "proteids" and as "albuminoids," terms which are now used in a more restricted sense, to apply to certain classes of proteins (see below).

They are almost all uncrystallizable, and only slightly dialysable; some are soluble in pure water, others only in presence of other substances, and others are insoluble in water. They are composed of carbon, hydrogen, oxygen and nitrogen. Most of them also contain sulfur, some contain phosphorus, others iron; and all contain small quantities of mineral salts. Their constitution is unknown, and no substance has as yet been obtained synthetically, which is identical with a natural protein, although substances have been so produced having many of the properties of the gelatins and albumoses.

A classification of the proteins ($\pi\rho\omega\tau\epsilon\tilde{\iota}o\nu$ = the first), based upon their constitution, is at present manifestly impossible, and any other classification can be only tentative. For a provisional classification some of the proteins arrange themselves naturally in well defined groups according to their products of decomposition and their solubilities, while others, of quite diverse characters, must be still arranged in the miscellaneous group of the "albuminoids." The classification which we will adopt is as follows:

I. **Albumens — Albuminous Substances** — (Eiweisskörper of the Germans).

a. *Albumins* — soluble in pure water; coagulated by heat. Serum albumin, ovialbumin, lactalbumin.

b. *Globulins* — insoluble in pure water, soluble in dilute solutions of neutral salts; coagulated by heat. Myosin, paraglobulin, fibrinogen, oviglobulins.

c. *Nucleoalbumens* — almost insoluble in pure water, or in solutions of neutral salts, easily soluble in slight excess of alkalies; contain phosphorus, and on decomposition by pepsin and hydrochloric acid yield pseudonucleins. Casein.

The above are distinguished as "native albumens" and exist in animal tissues and fluids. The members of the four remaining groups of this class are "derived albumens," products derived from the native albumens:

d. *Albuminates* — insoluble in water or in salt solution, except in

presence of acid or alkali; derived from native albumens by the action of acids or of alkalies. Acid-albumens, alkali-albumens.

e. *Albumoses — Propeptones* — soluble in dilute salt solution, precipitated by cold $HNO_3$, redissolved on heating.

f. *Peptones* — very soluble in water, readily dialysable, not coagulated by heat, nor by potassium ferrocyanid and glacial acetic acid.

g. *Coagulated albumens* — insoluble in water, or in salt solutions; obtained from native albumens by the action of heat, of strong mineral acids, or of enzymes, and do not regenerate the parent protein. Coagulated albumins and globulins, fibrin.

II. Proteids — on decomposition yield an albumen and some other substance.

a. *Haemoglobins* — yield an albumin or globulin and a crystalline pigment or chromogen.

b. *Glycoproteids* — yield a reducing substance (a carbohydrate). Mucins, amyloid, etc.

c. *Nucleoproteids* — yield a true nuclein, which, in turn, yields a xanthin base on decomposition. Nucleohiston, etc.

III. Albuminoids—proteins not included in one of the above classes. Keratins, elastin, collagen, etc., etc.

### ALBUMENS—ALBUMINOUS SUBSTANCES.

These substances are odorless and tasteless, generally amorphous, although certain vegetable albumens, serum albumin and an egg albumin have been obtained in crystalline form. They do not dialyse, or do so very slowly. Their solutions are laevogyrous. Their solutions may be evaporated at temperatures below that at which they coagulate, when they remain as white, or yellow, gummy masses, which redissolve unchanged in water. They have not been obtained entirely free from mineral salts. The native albumens suffer the change called "coagulation" when their faintly acid solutions are heated. They are thus converted into white, insoluble "coagulated albumens," from which the original substance cannot be regenerated. This change does not occur in alkaline solutions, and only partially in neutral solutions, and it is favored by the presence of about 1 per cent. of sodium chlorid. The "coagulation temperature" of an albumen, i. e., the temperature at which coagulation takes place, varies with different proteïns, and serves as one of the factors for their identification, although it varies within certain limits with the proportion of mineral salts present.

Neither the constitution, nor even the composition of these sub-

stances is known, yet from the products of their decomposition it is probable that they are highly complex amids or ureids. They all contain carbon, hydrogen, nitrogen, oxygen and sulfur, and some contain phosphorus. Their molecules contain at least two atoms of sulfur, as a part only of this element goes off in sulfid combination on boiling with caustic alkalies, the remainder only on fusion with alkali and nitre. As the proportion of sulfur which they contain does not exceed 0.3 to 2.2 per cent., they have large molecular weights. Their percentage composition is: C—50.6 to 54.5; H—6.5 to 7.3; N—15.0 to 17.6; S—0.3 to 2.2; P—0.42 to 0.85; O—21.50 to 23.50.

**Decompositions.**— The study of the decompositions of the proteins is of great importance, being the means by which a knowledge of their constitution and chemical relations must be sought for.

Oxidizing agents attack the molecule profoundly, yielding products far removed from the original substance: acids and aldehydes of the fatty and benzoic series, and their nitrils; and ketones, hydrocyanic acid, amido-acids, carbon dioxid and ammonia. On heating with baryta-water, under pressure at 150°–250°, an odor is developed which is both fæcal and ammoniacal; and ammonia, carbon dioxid, and oxalic and acetic acids are formed, along with a mixture of amido-acids as the principal product. These amido-acids belong to two classes: (1) **leucins,** or true amido-acids (p. 361), and (2) **leuceïns,** containing two atoms of hydrogen less than the corresponding leucins, and possibly amido-acrylic acids. The leucins and leuceïns appear to result from the hydrolysis of more complex substances called **glycoproteins,** because of their sweet taste, not to be confounded with the glycoproteids referred to below. On fusion with caustic alkalies, the proteins yield ammonia, mercaptan, fatty acids, and amido-acids, tyrosin, indole, and skatole.

When boiled with mineral acids, or better, with HCl and $SnCl_2$, the albumens are decomposed into amido-acids, hydrogen sulfid, ethyl sulfid, ammonia, and a series of nitrogen bases. Among the last-named are four well-defined substances, which are also produced during the tryptic digestion of albumen in the intestine, and which, containing six carbon atoms, are known as **hexon bases**: (1) **Lysin,** is diamido-caproic acid (p. 365). It is non-crystalline, soluble in water, dextrogyrous, and forms two chlorids and two silver compounds. It forms a crystalline compound with benzoyl chlorid in presence of alkali. (2) **Lysatin,** or **lysatinin,** $C_6H_{13}N_3O_2$, or $C_6H_{11}N_3O$, a homologue of creatin, or of creatinin (p. 336), which yields urea on decomposition by barium hydroxid. (3) **Arginin,** $C_6H_{14}N_4O_2$, a crystalline base, which also yields urea with barium hydroxid; and (4) **Histidin,** $C_6H_9N_3O_2$, a crystalline base, soluble in water, insoluble in

alcohol or in ether. Lysin, arginin, and histidin are also produced by decomposition of the protamins.

The **protamins**, first obtained from the melt of salmon and of other fish, by extraction with sulfuric acid of 1-2%, and purification, are the most important of the decomposition products of the proteins, because they are the substances most nearly related to the parent substance, whose chemical characters are definite. They have been considered as being the simplest of the proteins, but as they do not yield amido-acids on decomposition, as do the proteins, they are better considered as nuclei existing in the proteins. They are alkaline, basic, nitrogenous substances, which by tryptic digestion yield, first protamin-peptone, and afterwards the three hexon bases above-mentioned. Of the three protamins which have been described two are probably identical. **Salmin** and **clupein** (*clupea*=herring), from the melt of the salmon and of the herring, are the two referred to, $C_{16}H_{28}N_9O_2$ or $C_{30}H_{57}N_{17}O_6$. **Sturin**, from the melt of the sturgeon, probably has the composition $C_{36}H_{69}N_{19}O_7$. The protamins produce precipitates of histon (below) in ammoniacal solutions of albumins or of primary albumoses. They form salts with acids, which are soluble in water, insoluble in alcohol and ether. They are partially precipitated by salting with NaCl. They give the biuret, but not the Millon reaction, and are precipitated from their neutral solutions by phosphotungstic and picric acids, and by potassium ferrocyanid.

**Histon** is a substance obtained from the red corpuscles of goose blood, and from the protamins as above indicated, which has some resemblance to the albumoses. It does not coagulate by heat. With ammonia, in the absence of salts, it forms a precipitate, insoluble in excess. With $HNO_3$ it forms a precipitate, which redissolves on heating. The name "histon" has also been applied to other substances, and considerable confusion has been caused thereby. The substance met with in the urine in leukæmia and called histon differs from the above in being coagulable by heat.

The decomposition of proteins by **proteolytic enzymes** (πρωτεῖον= the first, λύσις=parting) results in the formation of albumoses, peptones, and amido-acids. Those changes occur in the processes of digestion, and will be discussed in the next section.

**Putrefaction** is the decomposition of dead protein material under the influence and as a result of the processes of nutrition of certain bacteria, and attended by the evolution of more or less fetid products. In order that it may occur certain conditions are necessary: (1) the presence of living bacteria, or of their germs; (2) the presence of moisture; (3) a temperature between 5° and 90° (41°–194° F.); (4) an atmospheric condition suitable to the growth of the bacteria. Some of the several species of bacteria which cause putrefaction are

ærobic, i. e., they require the presence of air for their development, while others are anærobic, i. e., they thrive best in the absence of oxygen. Proteins which have been deprived of moisture, either by drying or by the action of dehydrating agents, such as strong alcohol, do not enter into putrefaction unless water is supplied to them, when the process proceeds as usual. The temperature most favorable to putrefaction is about 40° (104° F.) High or low temperatures arrest putrefaction or prevent it, the former, if sufficiently high, permanently (if the material be protected from new bacteria) by destroying the vitality of the bacteria; the latter, even if extreme, only temporarily, and so long as the low temperature is maintained.

Putrefaction may, therefore, be prevented either (1) by the action of agents or substances which interfere with the development of bacteria (germicides and antiseptics); (2) by the exclusion of air; (3) by the exclusion of water; (4) by a temperature below 5° (41° F.) or above 90° (194° F.).

**Germicides are substances or agents which destroy bacteria and their germs.** Mercuric chlorid and heat are germicides.

**Antiseptics are substances which prevent or restrain putrefaction.** Antiseptics are either germicides, which prevent putrefaction by destroying the organisms which cause it, or are agents, which interfere with the development of these organisms without destroying their vitality. The salts of aluminium are antiseptic by reason of their chemical action on the proteins, although their germicidal powers are slight.

**Deodorizers, or air purifiers, are substances which destroy the odorous products of putrefaction.**

**Disinfectants are substances which restrain infectious diseases by destroying or removing their specific poisons.**

Putrefaction is attended by the breaking down and liquefaction of the material if it be solid; or its clouding and the formation of a scum upon the surface if it be liquid. The products of putrefaction vary with the conditions under which it occurs. The most prominent are: (1) inorganic products such as N, H, $H_2S$, $NH_3$, and simple organic compounds, such as $CO_2$ and hydrocarbons; (2) acids of the fatty series in great abundance, and acids of the oxalic and lactic series; (3) non-aromatic monamins and diamins, such as trimethylamin, putrescin, and certain of the ptomaïns; (4) aromatic products, among which are: (*a*) phenols, such as tyrosin, oxyaromatic acids, phenol, and cresol; (*b*) phenylic derivatives, such as phenyl acetic and phenyl propionic acids; (*c*) indole, scatole, scatole-carbonic acid, etc.; (*d*) ptomaïns of undetermined constitution, but belonging to the aromatic series; pyridin derivatives.

Under certain imperfectly defined conditions, buried animal matter

is converted into a substance resembling tallow, and called **adipocere**, which consists chiefly of ammonium palmitate, stearate, and oleate, calcium phosphate and carbonate, and an undetermined nitrogenous substance.

There occurs a decomposition of vegetable tissues under the influence of warmth and moisture, which is known as **eremacausis**, differing from putrefaction in that the substances decomposed are the carbohydrate instead of the azotized constituents, and in the products of the decomposition, there being no fetid gases evolved (except there be simultaneous putrefaction), and the final product is a brownish material (humus or ulmin).

**General Reactions.**—The albumens all respond to a great number of general reactions, which may be classified in three groups: I. Color reactions; II. Precipitations in an insoluble combination; *alkaloidal reactions;* III. Precipitations in a form which permits of easy resolution in the primitive form.

I. (1) A purple-red color when warmed to 70° (158° F.) with Millon's reagent. The reagent is made by dissolving, by the aid of heat, 1 pt. Hg in 2 pts. $HNO_3$ of sp. gr. 1.42, diluting with 2 vols. $H_2O$, and decanting after 24 hours. (2) A yellow color with $HNO_3$; changing to orange with $NH_4HO$ (xanthoproteic reaction). (3) A purple color with Pettenkofer's test (p. 527). (4) With a drop or two of cupric sulfate solution and liquor potassæ: a violet color (biuret reaction). (5) A solution of an albumen in excess of glacial acetic acid is colored violet and rendered faintly fluorescent by concentrated $H_2SO_4$ (Adamkiewicz' reaction). (6) With Fröhde's reagent (p. 485) solid albumens give a fine blue color. (7) If an alkaline solution of an albumin or a peptone be mixed with an alkaline solution of diazobenzosulfonic acid a red-brown or orange color is produced. If powdered Zn or sodium amalgam be added the color becomes a brilliant red (Petri's reaction). (8) Add to the albuminous liquid two drops of an alcoholic solution of benzoic aldehyde, then some $H_2SO_4$ diluted with an equal bulk of $H_2O$, and finally a drop of ferric sulfate solution: a dark blue color is produced either immediately on warming, or slowly in the cold (Reichl's reaction). (9) Albumins dissolve in boiling concentrated HCl (sp. gr. 1.19) with a violet-blue color, and coagulated albumins are similarly colored by boiling HCl. The color is the more distinct the purer the albumin. The reaction may be applied to the albumin coagulated from urine, after collection on a filter, and washing with water, alcohol, and ether (Liebermann's reaction).

II. The albumens are precipitated in an insoluble form by: (1) The concentrated mineral acids, notably $HNO_3$; (2) by potassium ferrocyanid in presence of acetic acid; (3) by certain organic acids in the

presence of concentrated solutions of NaCl or $Na_2SO_4$; (4) by tannin in acid solution; (5) by tungstates, or phosphomolybdic or phosphotungstic acid; (6) by potassium iodhydrargyrate, or potassium iodobismuthate in acid solution; (7) by solutions of the salts of Pb, Cu, Ag, Hg, U; (8) by chloral, picric acid, salicyl-sulfonic acid, phenol or trichloracetic acid.

III. Some of the albumens are precipitated in a form capable of resolution by solutions of certain salts, notably by the sulfates and phosphates of the alkaline metals, ammonium and magnesium.

The general characters of the several groups of albumens are as follows :

**Albumins**—are soluble in pure water, and are not precipitated therefrom by a small quantity of acid or of alkali, but are precipitated by excess of mineral acids and by metallic salts. They are coagulated by heat in the presence of neutral salts, but not by a boiling temperature in their absence. At 30° the addition of solid NaCl or $MgSO_4$ to saturation (salting) does not cause their precipitation until after the addition of acetic acid, when they separate. Salting their solutions with $(NH_4)_2SO_4$ to saturation causes their complete precipitation. (See Blood, Urine, Milk in next section; egg albumen below.)

**Globulins**—are insoluble in pure water, and precipitated from their solutions by dilution with a large quantity of water; soluble in dilute solutions of neutral salts, or in presence of slight excess of acid or of alkali, but precipitated from the latter solutions by neutralization; precipitated from their alkaline solutions by $CO_2$, but redissolved by excess of the gas. Their neutral solutions are partly or completely precipitated by salting with NaCl or $MgSO_4$, completely by salting with $(NH_4)_2SO_4$. They are coagulated by heat. They contain a smaller proportion of sulfur than the albumins (A=1.6–2.2%, G=about 1%). (See Blood, Urine, Milk in next section.)

**Egg-albumen**—The "white of egg" consists of a yellowish fluid, enclosed in a delicate network of connective tissue (keratin). The fluid portion, separated from the membrane by beating and filtration through muslin, is alkaline, sp. gr. 1.045, and of very complex composition; containing 850–880 p/m water, 100–130 proteins, 7 salts, and traces of fat, lecithins, cholesterol and a carbohydrate. The proteins of white of egg are at least five in number: 67 of the 100–130 p/m above referred to consist of two **globulins**, coagulated at 57.5° and 67°, partly precipitable by dilution with water, completely by salting with $MgSO_4$; three **albumins**, differing in coagulation temperatures; 67°, 72°, and 82°, and in specific rotary power: $[a]_D$= −25.8°, −34.2°, and −42.5°, all of which are lower than the value of $[a]_D$ for serum albumin, −62.6° to −64.6°. These albumins also differ

from serum albumin in that they appear in the urine when injected into the circulation, which serum albumin does not do. A crystalline albumin has been obtained from white of egg by removal of the globulins by partial salting with $(NH_4)_2SO_4$, slow evaporation of the solution at the ordinary temperature, and recrystallization. The carbohydrate above referred to appears to exist in the form of a **glycoproteid** (p.505 ), containing 15% of carbohydrate, and 1.18% of sulfur. **Ovimucoid** is a pseudo-peptone, constituting about 10% of the proteins of white of egg. It is not precipitated by mineral acids, except phosphotungstic acid, and is obtained, after removal of globulins and albumins by heat and acetic acid, by precipitation with alcohol.

**Nucleoalbumens**—are widely disseminated in animal and vegetable organs rich in cells, and also in solution in fluids. They contain phosphorus and traces of iron. They behave as acids, are almost insoluble in water, soluble in very weak alkaline solutions, very sparingly soluble in neutral salt solutions, and are not coagulated by heat. Their most characteristic property is that, upon peptic digestion they yield **para-** or **pseudo-nucleins** (p. 507). They resemble the nucleo-proteids, and the glycoproteids, but differ from the former in that they yield no xanthin bases on decomposition, and from the latter in that they yield no reducing substances under like conditions.

The **lecithalbumens** resemble the nucleoalbumens in that they contain phosphorus and do not yield xanthin bases, but on decomposition they yield lecithins (p. 319). They remain as insoluble residues of the peptic digestion of glandular tissues, and of the **ovivitellin** of the yolk of egg.

**Albuminates.**—Native albumens dissolve without change in dilute acid or alkaline solutions, and may be recovered therefrom, but with concentrated acids or alkalies, or by long contact with dilute solutions, derived products are formed, with loss of nitrogen, and even of sulfur. These **acid-** or **alkali-albumens** are jelly-like in consistency, soluble in warm water, almost insoluble in cold water, easily soluble in presence of a trace of acid or of alkali, and precipitable from these solutions by neutralization, but not coagulated by heat. Whether acid- and alkali-albumens are distinct substances, or one and the same, is doubtful. **Syntonin** is a form of acid-albumen produced from myosin by the action of HCl of 2 p/m by prolonged contact, or by short contact of the same acid in presence of pepsin. If concentrated, it is jelly-like in consistency, but differs from other acid-albumens in being insoluble in $NaH_2PO_4$ solution, and soluble in $CaH_2O_2$ solution.

**Albumoses** and **peptones** will be considered in the next section, under "Digestion."

**Coagulated Albumens**—are produced from some of the previously described proteins, either: (1) by heat; (2) by alcohol in presence of neutral salts. If the contact with alcohol be of short duration the protein is *precipitated*, and may be redissolved; if the contact be prolonged it is *coagulated* and permanently altered; (3) by long agitation of their solutions; (4) by the action of certain enzymes. But little is known of the nature of the change, or of the chemical characters of the products. These are white substances (fibrin, hard-boiled white of egg) insoluble in water, or in solutions of neutral salts, or in dilute acids or alkalies at the ordinary temperature. They are soluble by conversion into acid- or alkali-albumens by concentrated acids or alkalies, or by the same when dilute if aided by heat. They are acted upon by digestive enzymes and converted into albumoses and peptones. Although coagulated albumens are usually artificial products, except fibrin naturally coagulated, proteins having similar properties are met with in the liver and in other glands.

## PROTEIDS.

A proteid is a protein which is capable of being decomposed into an albumen and some other substance.

**Hæmoglobins**—yield an albumen and a crystalline pigment, or chromogen (see "Blood," in the next section).

**Glycoproteids**—on heating with dilute mineral acids, yield an albumen and a substance capable of reducing Fehling's solution, but no xanthin base (distinction from nucleo-proteids). They are divisible into two classes: (*a*) those which contain no phosphorus, and (*b*) those which contain phosphorus. The first class contains the **true mucins**, the **chondroproteids**, and the **mucoids**. The **true mucins** occur in connective and epithelial tissues, and in mucous secretions. They form slimy solutions in water, from which they are precipitated by acetic acid, and are not soluble in excess of the precipitant. When dry they are white or grayish, soluble in much water, to an acid solution, which is not coagulated by heat. They are not acted upon by the gastric juice. They contain no sulfur. When heated with dilute mineral acids they yield acid-albumen and a hexose called **mucose**. The **chondroproteids**, on decomposition by heating with dilute mineral acids yield an albumen and an ester-sulfuric acid, called **chondroitinsulfuric acid**, which contains a carbohydrate, and which is capable of precipitating the albumens. The principal members of the group are: **chondromucoid**, a constituent of cartilage, and **amyloid**, a pathological product met with in the kidney, liver and spleen in "amyloid degeneration." It appears in granules, resembling those of starch in gross appearance (hence the

name), amorphous, white, insoluble except in concentrated acids and alkalies, not dissolved by the gastric juice, colored red-brown by iodin, changing to violet on addition of $H_2SO_4$, colored bright-red by eosin, rose-red by anilin violet, and red by anilin green. The mucoids are non-phosphorized glycoproteids not belonging to one of the previous groups. They exist in the submaxillary saliva, intestinal mucus, vitreous, white of egg and umbilical cord. They are distinguished from the true mucins by not being precipitated by acetic acid.

**Phospho-glycoproteids**—are substances rich in phosphorus, which on decomposition by dilute acids yield a reducing substance (difference from nucleoalbumens), but no xanthin bases (difference from nucleoproteids). But two substances of this class have been described: icthulin, from the kidneys of the carp, and helico-proteid, from the mucous secretion of the snail.

**Nucleoproteids**—are substances intimately connected with the processes of cell-life, which occur, along with some of their components (nucleins) in glandular organs, liver, thymus, kidney, etc., in the melt of fish and the spermatozoa of higher animals, in pus, in the yeast-plant, etc., existing principally in the cell-nuclei, but also in the protoplasm. They are weak acids, insoluble in water, but forming soluble compounds with alkalies. They are rich in phosphorus, of which they contain 0.5–1.6%. They are decomposed by heating with dilute acids, or by peptic digestion, into an albumen, probably a globulin, and a true nuclein. By further decomposition the nuclein is decomposed into a further quantity of albumen and a nucleic acid, and by still further action the nucleic acid is decomposed into a xanthin base (pp. 356–359), a carbohydrate and a phosphorus acid, usually metaphosphoric acid. The best known of the nucleoproteids is nucleohiston, obtained from the thymus of the calf. It contains 3.025% of phosphorus and 0.701% of sulfur. Its solutions are decomposed by heat, with separation of a coagulated albumen, and it is also decomposed by HCl of 8 p/m, with separation of an albumen which dissolves in the acid, which differs from other albumens in being insoluble in excess of ammonia, and which has been called histon. In both cases a nuclein is the other product of decomposition. Nucleohiston is soluble in very dilute alkaline solutions, from which it is precipitated by acetic acid, and is insoluble in excess of the acid. It is also precipitated by alcohol, but not by salting with $MgSO_4$. It is supposed to play an important part in the coagulation of the blood (p. 553).

**Nucleins.**—The true nucleins, on decomposition by acids, yield albumens and nucleic acids, which in turn yield xanthin bases. They are obtained as insoluble or difficultly soluble residues on peptic

digestion of the nucleoproteids. They contain 5% and over of phosphorus, which on their decomposition is converted into metaphosphoric acid, and also traces of iron. By alkalies they are decomposed into albumens and nucleic acids. They are colorless, amorphous, very sparingly soluble in water, moderately soluble in dilute alkaline solutions, insoluble in alcohol and ether, not disolved by gastric juice or by dilute acids, and behave as rather strong acids. They give the biuret and the Millon reactions, and readily take up basic pigments from aqueous or alcoholic solution.

**Pseudo-, or para-nucleins** — differ from the true nucleins in yielding no xanthin bases on decomposition. They are obtained as sparingly soluble residues on peptic digestion of nucleoalbumens or phospho-glycoproteids. They are rich in phosphorus, which they also give off as metaphosphoric acid. They are amorphous, insoluble in water, alcohol and ether, soluble in dilute alkaline solutions, insoluble in dilute acids. Some of them, on decomposition by acids, yield reducing substances, but those best known do not.

**Nucleic acids** — are obtained by decomposition of nucleins by alkalies. On decomposition they yield a xanthin base, a carbohydrate and metaphosphoric acid. There is at least one acid corresponding to each of the four bases, xanthin, hypoxanthin, guanin and adenin, and probably others containing two of these bases. They also differ in the nature of the carbohydrate which they contain, which in some is a hexose, in others a pentose, and still others contain both hexoses and pentoses. They are all amorphous, white, acid, almost insoluble in alcohol or in ether, and readily soluble in dilute alkaline solutions. They give neither the biuret nor the Millon reaction. They form precipitates in solutions of albumens, by regeneration of nucleins. The guanyl acid, obtained from pancreas, yields 36 % of guanin, 30 % of pentose, and 18 % of phosphoric anhydrid.

## ALBUMINOIDS.

This is a miscellaneous collection of those proteins which are neither albumens nor proteids. About the only character which they have in common is that they are insoluble in the solvents of the members of the preceding groups. They, for the most part, occur in connective tissues, cartilage, bone, epidermic tissues, etc.

**Keratins** — occur in epidermis, hair, nails, horn, hoofs, feathers, tortoise-shell, and other epidermic tissues, in brain and nerve tissue (neuro-keratin) and in the membrane of eggs. They vary in composition, containing from 1.6 % to 5.0 % of sulfur, the maximum of that element being found in human hair, which yields a sulfid even to boiling water, a fact utilized in lead and other metallic hair-

dyes, which form colored sulfids. There are several keratins, which are amorphous, insoluble in water, alcohol, ether, acids, gastric juice or trypsin, slowly soluble in alkalies. When heated with water under pressure to 150°–200°, they dissolve, but do not gelatinize. Their products of decomposition are similar to those of the albumens, except that their sulfur is more easily split off. They give the xanthoproteic and Millon reactions, sometimes imperfectly.

**Elastin** — occurs in elastic tissues, notably the ligamentum nuchae. Its sulfur content is small, 0.27–0.66 %. When dry, it is a yellow powder, insoluble in the usual solvents, only slowly soluble in boiling, concentrated caustic potash, or concentrated sulfuric acid, soluble in hot HCl. When heated with water under pressure, or by boiling with dilute acids, or by the action of proteolytic enzymes, it is decomposed into two albumoses, both soluble in water, and differing from each other in that one, protoelastose, is precipitated by heat, by mineral acids, or by acetic acid and ferrocyanid, while the other, deuteroelastose, is not so precipitated.

**Collagen — Ossein** — is the principal constituent of the fibers of connective tissue, bones, tendons and cartilage. When dry it is amorphous, yellow, hard, insoluble in water, dilute acids or alkalies. Macerated in dilute acids it swells and become pliable. If previously heated to 70° with water, it is soluble in the gastric and pancreatic juices. Its products of decomposition are similar to those of the albumens, but it yields a large proportion of glycocoll, which is not produced from the true albumens. In putrefaction no tyrosin, indole or skatole is formed. The tannins combine with collagen to form a tough, hard, imputrescible material which constitutes leather. When boiled with dilute acids, or when heated with water under pressure, collagen is converted into gelatin or glue. This is a translucent material, white to brown, according to purity, which swells, but does not dissolve in cold water, soluble in hot water, the solution gelatinizing, i.e., forming a jelly-like mass, on cooling, or if more concentrated, the solution on cooling becomes solid and hard (glue). Gelatin gives the biuret reaction, but not the Millon reaction. It is dissolved by gastric and pancreatic juices, probably with formation of two albumoses, and later, of peptone.

Other albuminoids are: Reticulin, from connective tissues, intestinal mucous-membrane, liver, spleen, kidney, lungs; contains phosphorus. Chitin constitutes the albuminoid portion of the hard parts of insects. Spongin is the principal organic constituent of sponges. Conchiolin is the albuminoid of the shells of molluscs. Fibroïn and sericin are the principal constituents of raw-silk. Korneïn is obtained from coral zoöphytes. Ichthylepidin exists, along with collagen, in fish-scales.

## VEGETABLE PROTEINS.

Proteins exist in the liquids, and particularly in the reproductive organs of plants. They resemble the animal proteins in their general properties, and in the products of their decomposition by dilute acids and by digestive enzymes. They have been classified into four groups: (1) vegetable albumins; (2) vegetable globulins; (3) gluten proteins; and (4) vegetable caseins.

The classes of **vegetable albumins** and **vegetable globulins** are not sharply differentiated, as the latter are not entirely insoluble in pure water. Both are coagulated by heat. The effect of sodium chlorid upon solutions of vegetable globulins also varies with the proportion of salt present; a small amount causing a precipitate, which redissolves in a larger proportion, and is again precipitated by a further addition of salt. Wheat flour contains 0.26 to 0.30% of protein coagulable by heat, and 1.55 to 1.90% of protein material not so coagulable. **Conglutin**, a protein obtained from the lupines and from almonds, has most nearly the characters of the globulins, being soluble in salt solutions of 5 to 10 per cent., and precipitable therefrom by dilution with water. A similar globulin accompanies legumin in peas.

**Gluten** is the protein material existing in wheat and other cereals, which remains insoluble and forms a soft, but tough, elastic paste, when the flour is kneaded in a stream of water upon a fine seive. It constitutes about 78% of the total proteins of wheat. It is made up of at least four factors. On extracting it with alcohol, gluten casein (below) remains as an insoluble residue; and the solution contains **gliadin**, **mucedin**, and **gluten-fibrin**, which differ from each other principally in their solubility in water and in alcohol of varying degrees of concentration. Maize also contains a protein called **zein**, which resembles gluten-fibrin, but is not identical with it.

The **vegetable caseins** are insoluble in pure water and in salt solutions, but are readily soluble in dilute acids or alkalies, and are coagulated by heat. **Legumin** is a vegetable casein existing in peas, beans, and other leguminous seeds. **Gluten casein** occurs in cereals. **Aleurone corpuscles**, or **protein granules** are minute rounded masses which accompany, and sometimes replace starch granules in various grains and nuts, notably in Brazil nuts. They resemble starch-granules in shape and appearance, but are colored brown by iodin, and contain 9.36% of nitrogen. They contain more than one protein, probably three, one of which is a vegetable casein which may be obtained from Brazil nuts in the form of well-defined crystals, by treatment of the finely-divided tissue with ether, and then with water, from which the crystals are deposited by subsidence.

## PHYSIOLOGICAL CHEMISTRY.

The adjective "physiological" is here used in its proper sense. Physiology (φυσιολόγος=discoursing of nature) is defined as "the sum of scientific knowledge concerning the functions of living things." Chemistry has been defined as "that branch of science which treats of the composition of substances, their changes in composition, and the laws governing such changes." Therefore physiological chemistry has to do with the composition and changes in composition of living things, *whether they be in a normal or in an abnormal condition.* The medical tendency to distinguish between "physiological" and "pathological" chemistry, the former being considered as a branch of physiology, and the latter as a division of pathology, besides involving a solecism, is undesirable for four reasons: (1) The methods by which tissues and fluids are obtained from otherwise normal animal bodies for investigation are frequently such that they establish a pathological condition, and the extent to which the material so obtained is thus modified from the normal must always be taken into consideration in interpreting the results. (2) A solution of a doubtful question in normal physiological chemistry is frequently obtained by establishing a pathological condition, or by taking advantage of one occurring as a result of disease or accident, and comparing the composition of a tissue or fluid under these conditions with those from a normal subject. (3) Pathological chemical composition and processes are variations, either qualitative or quantitative, from the normal, and can therefore only be studied by comparison with the normal, hence the study of "physiological" and "pathological" chemistry must go hand in hand. (4) The substances most nearly concerned in the functions of life are of the most complex chemical constitution, and their study requires a high degree of chemical knowledge, patience and ingenuity. The physiological chemist must be a thoroughly trained chemist, equipped with sufficient medical knowledge for the study of this *chemical* specialty, not a physiologist or a pathologist who dabbles in chemistry.

Vegetable physiological chemistry is particularly of interest to the agriculturist, animal physiological chemistry to the veterinarian and the physician. Only the latter branch will be here considered.

The subject may be divided into two sections: (1) the study of the properties, physical and chemical, of the various substances (proximate principles) which occur in living bodies; (2) that of the chemical changes, chemical processes, which take place in living organisms. The first division is a part of pure chemistry, and has

been considered in the preceding pages, the more important subjects of the second division will be discussed in the following.

One of the most striking differences between unorganized and organized nature is that in the former those changes which occur are almost entirely physical, while in the latter they are essentially chemical. Water passes through the conditions of solid, liquid and vapor, the rocks are eroded, the air varies in temperature and moves from place to place, all physical changes, but neither water, rock nor air suffers change of composition. But in vegetable and animal bodies changes in composition are constant and essential to life; the atoms of carbon, hydrogen, nitrogen and oxygen are in constant passage from one form of combination to another. Indeed life may be said to consist of chemical reactions; and the physical processes and conditions of and in the bodies of vegetables or animals occur or exist that these reactions may take place.

Energy, like matter, is indestructible, and cannot be created. The sum of potential and kinetic energy in the universe is immutable. The relative proportions of the two forms of energy is constantly varying. Every chemical change involves the conversion of potential into kinetic energy, or the reverse. The atoms of carbon and oxygen uncombined with each other, are endowed with a definite amount of potential energy, which is converted by their union into a definite and equivalent amount of kinetic energy, which is manifested and is measurable as heat, which may in turn be converted into other forms of energy. Once united, the carbon and oxygen have lost the potential energy which they possessed while ununited, and, as energy cannot be created, they can only recover it by some second reaction in which an equivalent quantity of kinetic energy becomes potential in separating the atoms once more. This cycle may be mathematically expressed by the equations: $C+O_2+\text{potential}=CO_2+\text{kinetic}$, and $CO_2+\text{kinetic}=C+O_2+\text{potential}$. As animal bodies are constantly converting potential energy into the kinetic forms of heat, motion, etc., they must be supplied with potential energy from without, which, in its turn, has been derived from some form of kinetic energy.

The source of this energy is the kinetic energy of the sun's rays. The green parts of plants owe their color to the presence of a pigment called **chlorophyll**, which is only present in leaves and stems exposed to sunlight. In the daytime, and while exposed to sunlight, plants absorb carbon dioxid from the air and give off oxygen; during the night they absorb oxygen and evolve carbon dioxid; but in very much less quantity. Plants also absorb water and ammonia. From these comparatively simple substances the plants form carbohydrates

and proteins under the influence of the kinetic energy of the sun's rays, which thereby becomes potential. In the animal body the carbohydrates and proteins are converted into carbon dioxid, water and urea (the last-named yields ammonia by fermentation) and their potential energy becomes kinetic. The tissues of the plant are, directly or indirectly, the food of the animal, and the excreta of the animal constitute the food of the plant. The chemical processes in the vegetable are essentially synthetic, producing complex substances from simpler forms of combination; but analytic processes also occur in vegetables, as that which results in the evolution of oxygen, above referred to. The processes of animal-nature are, on the other hand, essentially analytic, complex combinations being reduced to simpler forms; but synthetic processes also occur in animal bodies, as in the formation of hippuric and the ester-sulfuric acids.

The composition of various articles used as foods, the effects upon them of different methods of preparation, and the relative proportions in which the several components should be contained in properly adjusted dietaries, are, like the composition of air under varying conditions, important subjects of inquiry for the hygienic chemist. In this place, however, we will content ourselves with the statement that the materials required for the chemical processes taking place in the body, and contributing to the growth or repair of the tissues, and to the production of kinetic energy, are of six classes: (1) Oxygen, (2) water, (3) mineral salts, (4) carbohydrates, (5) fats, (6) proteins. Of these, oxygen, water and salts pass into the system by the physical processes of diffusion and absorption, without the necessity of any preliminary chemical treatment. But the fats, the carbohydrates, and, notably, the proteins, require more or less extensive chemical modification from the forms in which they are taken into the mouth before they can be absorbed. This is the purpose of digestion.

Chemical processes occurring in the body may therefore be divided into the two classes of preparatory and essential. The former including the processes preparatory to absorption which occur in the alimentary canal; the latter the metabolism of the tissues, cells, and fluids of the body.

## DIGESTION.

### SALIVA.

The saliva is a mixture of the secretions of several glands: The **submaxillary saliva**, which may be obtained by inserting a canula in Wharton's duct, is a clear, thin, colorless, slightly viscid, frothy,

alkaline liquid; sp. gr. 1002 to 1003; containing 3.6 to 4.5 p/m of solids. These solids consist of mucin, a trace of albumin, a diastatic enzym, KCl,NaCl,$Na_2HPO_4$,$Mg_2H_2(PO_4)_2$,$NaHCO_3$,$CaH_2(CO_3)_2$, and KCNS. In the dog, the saliva obtained by nerve-excitation differs according to the nerve supply which is irritated: the **chorda tympani**, or **cerebral saliva** contains 12 to 14 p/m of solids; sp. gr. 1004 to 1005.6; is more abundant and contains less mucin than the **sympathetic saliva**, which contains 16 to 28 p/m of solids; sp. gr. 1007.5 to 1018.

The **sublingual saliva** is clear, viscid, alkaline, and contains mucin, a diastatic enzym and potassium thiocyanate.

The **parotid saliva**, which may be obtained by a canula inserted into Steno's duct, is a thin liquid, usually alkaline, but sometimes neutral, or even faintly acid; sp. gr. 1003 to 1012. It contains 5 to 16 p/m of solids, among which are a small quantity of albumin and a diastatic enzym, but no mucin. Potassium thiocyanate is sometimes present.

**Mixed saliva** consists of the above, plus the secretions of the mucous glands. It is colorless, tasteless, odorless, opalescent, frothy, slightly viscid; and cloudy from the presence of epithelium, mucus corpuscles, leptothrix, and food particles. On exposure to air it becomes more cloudy and covered by a pellicle, which consists of calcium carbonate. Its reaction is alkaline, the average alkalinity being equal to 0.8 p/m of $Na_2CO_3$, and diminishing, sometimes to acidity, after meals. Sp. gr. 1002 to 1008. It contains 5 to 10 p/m of solids, of which the organic constituents are albumin, mucin, urea, thiocyanate, and two enzymes, **ptyalin** and **glucase.** According to an analysis of Hammerbacher, it has the composition: Water: 994.2; mucus and epithelium: 2.2; soluble organic constituents: 1.4; thiocyanate: 0.04; salts: 2.2. The composition of the ash in 1,000 parts is: $K_2O$–457.2; $Na_2O$–95.9; CaO and traces of $Fe_2O_3$–50.11; MgO–1.55; $SO_3$–63.8; $P_2O_5$–188.48; Cl–183.52.

**Enzymes** are a class of physiologically important substances, some of vegetable origin, like diastase, emulsin, papaïn and myrosin, others of animal origin, like ptyalin, pepsin and trypsin, concerning whose chemistry but little is known beyond the effects which they produce. They are sometimes referred to as **soluble** or **unorganized ferments** in comparison with, yet in distinction from the true ferments, such as the yeast plant, mother-of-vinegar, etc., which are vegetable organisms, while the enzymes are, apparently, chemical compounds. They are protein in character, precipitated by alcohol and by lead acetate, not diffusible, and are destroyed by the temperature of boiling water. Their prominent characteristic is their power, when present even in small quantity, of setting up a chemical change

in certain other substances. Some, called **amylolytic** or **diastatic enzymes**, convert starch into maltose or into glucose; some, referred to as **proteolytic enzymes**, convert albumins and globulins into albumoses and peptones; others cause the saponification of fats; others invert cane sugar or maltose; while still others set up a variety of other actions (emulsin, myrosin, chymosin, etc.). Their activity is only manifested within narrow ranges of temperature, the body temperature being the most favorable for the action of the digestive enzymes. Their activity also diminishes with the accumulation of their products, and is finally arrested thereby. It is also impeded by putrefaction. The presence of 1 in 200 of chloroform, which completely arrests fermentations, favors the action of enzymes by preventing putrefaction, and chloroform-water is frequently used to prevent putrefaction in experimentation extending over considerable time. Some cells produce **zymogens**, i.e. substances which are not enzymes, but which, under certain influences, as by combination with acid, generate enzymes. Most enzymes are soluble in glycerol.

**Saliva enzymes.** — The saliva contains two enzymes: one amylolytic, converting hydrated starch into maltose and iso-maltose (p. 273), which exists in human saliva at all ages, but not in the saliva of the carnivora, known as **ptyalin.** The other **glucase**, present in the saliva in small amount only, which converts maltose into glucose. Ptyalin has not been obtained in a condition of purity. Gautier's method gives the product most nearly approaching purity: the saliva is treated with a large quantity of strong alcohol; the precipitate is collected and redissolved in water; albumens are precipitated by mercuric chlorid and separated by filtration; the excess of mercury is removed by hydrogen sulfid; the salts are removed by dialysis; and the ptyalin again precipitated by alcohol.

The activity of the amylolytic action of saliva is directly proportionate to the quantity of the enzymes present. The most favorable reaction is a very faintly acid one, due to carbonic acid, and the activity is diminished by either an alkaline reaction or an acid one due to mineral acids. The action is completely arrested by the presence of 0.03 p/m of HCl. The most favorable temperature is 40° (104° F.). The accumulation of its products interferes with the continuance of the action, and it is therefore more rapid and extensive when it takes place in a dialyser than when it occurs in a glass vessel. On the other hand, it is favored by the presence of peptones. The presence of 0.05 p/m of $HgCl_2$ arrests the action, and a like result is produced by 5 p/m of $MgSO_4$, while 0.25 p/m of the latter salt favors the action.

The total quantity of saliva secreted in 24 hours has not been

directly determined in the human subject. It is estimated at from 600 to 1,500 cc. During mastication 1 gram of salivary gland produces 13 grams of saliva per hour. The quantity is increased by pilocarpin and by eserin, and diminished by atropin. Many metallic salts are eliminated by the saliva, e. g., those of mercury and potassium, and the bromids and iodids; others do not appear in the saliva, e. g., the salts of iron. The quantity is pathologically increased in poisoning by the soluble mercurials, the mineral acids and alkalies; in neurotic conditions, and in inflammatory diseases of the mouth. It is diminished in febrile diseases, in diabetes, sometimes in nephritis, and under violent psychic emotions.

**Salivary calculi** are rarely met with, varying in size from mere granules to masses weighing 18.6 grams. They consist principally of calcium carbonate, with some tricalcic phosphate, and from 50 to 368 p/m of organic matter.

## GASTRIC JUICE AND GASTRIC DIGESTION.

While at rest, in the intervals between digestion, the stomach contains only a thick, slimy, neutral, or even alkaline liquid, the gastric mucus, or **succus pyloricus**, so-called because it is the product of glands located principally at the pyloric end. The true **gastric juice** is produced only during digestion, or by stimulation of the secreting glands, the fundus, or pepsin glands, by "chemical" or "psychic" action. The gastric juice of man has not been obtained free from saliva. Mixed with saliva, it has been obtained in cases of traumatic (Beaumont), or surgical (Richet) gastrostomy. From animals it may be obtained pure by the establishment of gastric and œsophageal fistulæ.

The gastric juice is a slightly cloudy, almost colorless liquid, sp. gr. 1001 to 1010, having an acid taste and a strongly acid reaction. It deposits a sediment, which, unmixed with food particles, contains gland cells and nuclei, mucus corpuscles and altered cylindrical epithelium.

According to an analysis by Schmidt of human gastric juice, mixed with some saliva, it contains: Water –99.44, solids –0.56, free hydrochloric acid, 0.25. The solids consist of: organic substances (pepsin, etc.) –0.32, NaCl –0.14, KCl –0.05, $CaCl_2$ –0.006, phosphates of Ca, Mg, and Fe –0.015. Among the organic constituents are a small quantity of a nucleoproteid, a mucin, an albumose (?), and two zymogens which produce the two enzymes, **pepsin** and **rennet.** The most important constituents are the free acid and the zymogens.

It is now established that the **free acid** of the normal, unmixed

gastric juice is hydrochloric acid. During digestion lactic acid or butyric or acetic acid may be present. They are, however, not products of secretion, but are derived from constituents of the food. The amount of hydrochloric acid present varies in different animals, and, within narrower limits in the same animal at different times. The gastric juice of the dog contains from 2 to 6 p/m, that of the cat about 5 p/m. The proportion usually accepted as present in human gastric juice is 2 to 3 p/m; but it is probable that this estimate is too low.

The exact mechanism of the formation of the gastric hydrochloric acid is unknown. That it is derived from the chlorids of the blood is most probable, although it may result from decomposition of chlorinated amids, which have been found to exist in gland tissues. A fact which supports the supposition of the derivation from the chlorids is that if dogs be given a diet from which chlorids are excluded the hydrochloric acid, after a time, ceases to be formed, while pepsin continues to be secreted; and if now the animal be given bromids, iodids, or chlorids, the gastric juice will contain hydrobromic, hydriodic, or hydrochloric acid, as the case may be. The most probable supposition with regard to the method of formation of the acid from the chlorids is that it is produced by chemical action, the chlorids being decomposed by the free carbon dioxid (or carbonic acid) in the blood, according to the equation: $2NaCl+CO_2+H_2O=Na_2CO_3+2HCl$; or it may be the result of decomposition of calcium chlorid by the disodic phosphate of the blood: $2Na_2HPO_4+3CaCl_2=Ca_3(PO_4)_2+2HCl+4NaCl$. The former reaction is the more probable, because of the generation of alkali, mentioned below, during stomach digestion. It has been suggested also that the chlorids may be decomposed by an electrolytic action resulting in reactions such as: $2NaCl=Na_2+Cl_2$; $Na_2+H_2O+CO_2=Na_2CO_3+H_2$, and $H_2+Cl_2=2HCl$. There is, however, no proof of the occurrence of such action. The reaction $2NaCl+CO_2+H_2O=Na_2CO_3+2HCl$ implies the formation of a quantity of alkali equivalent to the amount of acid generated, which should manifest itself somewhere in the system to a degree proportionate to the quantity of acid formed at different times. It is supposed that the alkali thus produced enters into combination with the lecithalbumens which exist in gland cells. Whether this is the case or not, it is known that the acidity of the urine varies inversely with the activity of hydrochloric acid formation; and that the urine may even become alkaline during the greatest activity of stomach digestion and in hyperchlorhydria.

Pepsin and Pepsinogen.—Pepsin exists in the gastric juice of all vertebrates, and at all ages. It has not been obtained in a condition of purity, the nearest approach thereto being the product of

Brücke's method: The mucous membrane is extracted with water containing phosphoric acid; the filtered extract is treated with lime water; the precipitate of tricalcic phosphate containing the pepsin, which it carries down mechanically, is dissolved in dilute hydrochloric acid, and the solution freed from salts by dialysis. For digestion experiments an extract made by macerating the mucous membrane in glycerol containing 1 p/m of HCl and filtered after 8–14 days, may be used. As prepared by Brücke's method pepsin is soluble in water and in glycerol, from which it may be precipitated by alcohol. It does not give the albumen reactions. In aqueous solution its activity is rapidly destroyed by boiling, more slowly in neutral solution at 55°, in acid solution at 65°, at 70° in presence of peptones, and quite rapidly even at 38–40° in presence of very small quantities of alkaline carbonates. When dry it may be heated to 100° without decomposition. The characteristic property of pepsin is that it dissolves albumens, with formation of albumoses and peptone, in acid, but not in neutral or alkaline solutions.

**Pepsinogen**, or **propepsin**, is the zymogen from which pepsin is formed by contact with hydrochloric acid, and is probably produced by the chief cells of the fundus glands. The mucous membrane of the fasting stomach yields to dilute hydrochloric acid an actively digesting extract, even after treatment with 1% sodium carbonate solution, at 40°, which very rapidly destroys the activity of pepsin, but acts only very slowly upon pepsinogen. It has been supposed that pepsinogen and hydrochloric acid combine chemically together to form a definite compound, the active material of the gastric juice, which has been called **pepsohydrochloric acid.**

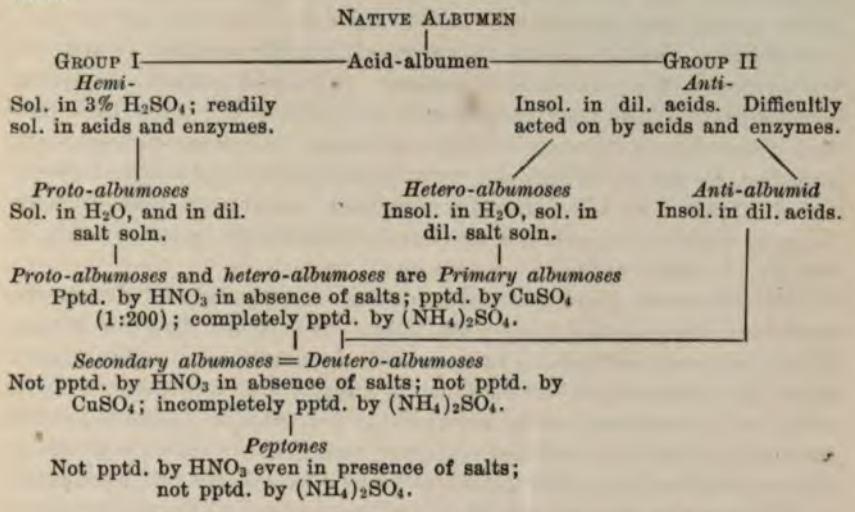
As has been stated above, the characteristic reaction of pepsin is its power of dissolving albumens in acid solution. If a fragment of coagulated white of egg be immersed in HCl of 2-4 p/m at 40° it is not affected, but if a trace of pepsin be also present, the edges of the fragment are soon rounded, and the material becomes transparent, and finally dissolves. A similar effect is produced more rapidly and at a lower temperature (20°) with fibrin. A similar action, but slower, occurs with acids other than hydrochloric, diluted strong acids acting better than weak acids. The rapidity of the action is also affected by other conditions: it is more rapid if the products of the action be removed by dialysis than if they be allowed to accumulate; and it is less rapid in presence of salicylic acid, metallic salts, alkaloids, phenol, sulfates, or of alcohol in greater proportion than 10%. The most favorable temperature is 40°, and the most advantageous proportion of HCl about 2.5 p/m.

The conversion of albumen into peptone is by no means a simple process. The first stage consists in the conversion of albumen into

acid-albumen (syntonin, p. 504). This then undergoes gradual cleavage by hydrolysis, with diminution of molecular weight, and increase in the degree of diffusibility, until the end product is reached. Intermediate between the acid-albumens and the peptones, a series of substances, called albumoses, or propeptones are formed, which differ from the albumens in their behavior towards nitric acid and towards ferrocyanid. With nitric acid at the ordinary temperature, or with acetic acid and potassium ferrocyanid, they form precipitates which redissolve on the application of heat, and are reprecipitated on cooling. From the peptones they differ chiefly in being precipitated from their solutions by salting with ammonium sulfate, although those albumoses most nearly related to the peptones, the deutero-albumoses, are only partially precipitated in that manner. The albumoses are divided into two groups: the primary albumoses, including the proto- and hetero-albumoses (below), and the secondary, or deutero-albumoses; the former being more nearly related to the native albumens, the latter more nearly to the peptones. They differ from each other principally in their behavior towards nitric acid: the primary albumoses are precipitated by nitric acid, even in the absence of neutral salts, while the secondary albumoses are not precipitated under these circumstances, although they are precipitated by nitric acid in presence of neutral salts. They also behave differently towards ammonium sulfate, which precipitates the primary albumoses completely, the secondary albumoses only partially. The primary albumoses are also precipitated by cupric sulfate (1:200) which does not precipitate the secondary albumoses. In the process of cleavage of the native albumens by the action of proteolytic enzymes, or of dilute mineral acids alone, the first products form two groups, differing from each other in the facility with which they are further acted upon by the acids and enzymes: (1) the hemi-group, from which the proto-albumoses are derived, being readily soluble in dilute acids, or by the action of enzymes and acids; and (2) the anti-group, from which the hetero-albumoses and antialbumose, the latter insoluble in acids, are derived; which are insoluble in acids except in presence of enzymes, and then more slowly than the hemi-compounds. The albumoses obtained from the several native albumens are not identical. From each parent substance different proteoses are formed, which are distinguished as albumoses, globuloses, vitelloses, caseoses, etc. The final products of the action are the peptones. These are extremely soluble in water, hygroscopic, highly diffusible, are not precipitated by ammonium sulfate, nor by nitric acid, even in solutions saturated with salts, nor by the usual precipitants of the albumens, except phosphotungstic and phosphomolybdic acids, mercuric chlorid, strong

alcohol, and tannin. They are not coagulated by heat. They give the biuret reaction (p. 525).

The changes above described may be thus expressed in tabular form


NATIVE ALBUMEN
Acid-albumen
GROUP I
Hemi-
Sol. in 3% $H_2SO_4$; readily sol. in acids and enzymes.
GROUP II
Anti-
Insol. in dil. acids. Difficultly acted on by acids and enzymes.
Proto-albumoses
Sol. in $H_2O$, and in dil. salt soln.
Hetero-albumoses
Insol. in $H_2O$, sol. in dil. salt soln.
Anti-albumid
Insol. in dil. acids.
Proto-albumoses and hetero-albumoses are Primary albumoses
Pptd. by $HNO_3$ in absence of salts; pptd. by $CuSO_4$ (1:200); completely pptd. by $(NH_4)_2SO_4$.
Secondary albumoses = Deutero-albumoses
Not pptd. by $HNO_3$ in absence of salts; not pptd. by $CuSO_4$; incompletely pptd. by $(NH_4)_2SO_4$.
Peptones
Not pptd. by $HNO_3$ even in presence of salts; not pptd. by $(NH_4)_2SO_4$.

The peptone which is the final product of peptic digestion is called **ampho-peptone**, and is further decomposable by tryptic digestion (p. 533) into **anti-peptone** and **hemi-peptone**, which differ from each other in that by continued tryptic digestion, the latter is further decomposed with formation of amido-acids, leucin, tyrosin, etc., while the anti-peptone remains undecomposed.

While the peptones are the end-products of the action of digestive enzymes upon the proteins, they do not exist in the normal blood, not even in that of the portal vein during active digestion of proteins, nor is the protein-content of the chyle appreciably increased during their absorption. It is supposed that the peptones, and albumoses, are converted into serum-albumin, or other form of protein combination in the gastro-intestinal mucous membrane, by some process in which the leucocytes play a part.

Pepsohydrochloric acid exerts the following actions upon other substances: the nucleoalbumens and nucleoproteids are decomposed, leaving residues of pseudonuclein or of nuclein, which are unacted upon (p. 506), while the albumens are dissolved as peptones. Glycoproteids are similarly decomposed, with formation of peptones and reducing substances. Collagen is slowly digested, by conversion, first into gelatin, then into proto- and deutero-gelatoses, and finally into peptone. Keratin is not acted upon; elastin only very slowly. Animal and vegetable cell membranes, being made up of keratin and

elastin in varying proportion, are differently acted upon according to their tenure of their two constituents. The connective tissue of the panniculus is dissolved. Haemoglobin is decomposed with formation of hæmatin and acid-albumen. Fats and carbohydrates are unacted upon, except that saccharose may be inverted.

**Chymosin and Chymosinogen**—are the milk-curdling enzym and the zymogen from which it is derived. The enzym exists in normal human gastric juice, and is the active constituent of rennet, the salted and dried fourth stomach of the calf, used by cheese-makers. Its function is rapidly destroyed by a temperature of 60°, and slowly (in 48 hours) at 40°. Its characteristic property is that of coagulating milk, or a solution of casein containing calcium salts in neutral or faintly alkaline solution.

The observed abnormal variations in composition of the gastric juice relate principally to the free acid. Free hydrochloric acid may be absent (anachlorhydria) in neurasthenic conditions, in chronic gastritis, in carcinoma of the stomach, and in the secondary stage of corrosion by mineral acids or alkalies. It may be present in subnormal quantity (hypochlorhydria) in subacute or chronic gastritis, ulcer of the stomach, dilatation, and the earlier stages of carcinoma. Or the amount may be greater than the normal (hyperchlorhydria) in neurasthenic patients, or, sometimes, in carcinoma. When the amount of free hydrochloric acid is subnormal, fermentative changes, usually prevented by the antifermentative and antiseptic action of the pepsohydrochloric acid, are set up, with the formation of lactic and even of acetic and butyric acids, with liberation of hydrogen and consequent eructations of gas and heartburn. These organic acids may also frequently be present in the stomach, having been introduced with the food; lactic acid exists in sour-krout, in pickles, and in all kinds of bread; acetic acid is the acid of vinegar; and free butyric acid may be present in butter. It appears to have been demonstrated that in most cases of carcinoma of the stomach lactic acid is present in the stomach contents in greater amount than can be accounted for by the test-meals which have been used. Pepsin is very rarely absent, only after complete destruction of the pepsin glands by the action of corrosives. Chymosin is absent in carcinoma, chronic gastric catarrh and atrophy of the mucous membrane. Abnormal constituents, not introduced by the mouth, may also be present: urea and ammonium carbonate in uræmia, acetone in acetonurea, the constituents of the blood, or hæmatin, as the result of hemorrhage into the stomach, and, frequently, the constituents of the bile, by regurgitation; also arsenic and morphin when they have been taken in poisonous dose by channels of absorption other than the mouth.

**Examination of Stomach Contents.**—Usually it is desirable to obtain the gastric secretion as free as possible from the constituents of food articles. With this object the stomach contents are collected after the stomach has been washed out, and the secretion of gastric juice stimulated by a "test-meal." Many such have been recommended, of which probably the most serviceable is that of Boas, consisting of a tablespoonful of rolled oats and a quart of water, boiled down to a pint, to which a little salt may be added. The stomach contents are collected one hour after the meal has been taken.

**Total Acidity.**—Four factors may contribute to the acid reaction of the gastric contents: free hydrochloric acid, hydrochloric acid in protein combination (see below), organic acids, and acid salts. The sum of these, or of such of them as may be present, constitute the total acidity. This is determined by titrating 10 cc. of the filtered gastric contents with N/10 (one-tenth normal) caustic soda solution, using phenol phthaleïn as an indicator. As each cc. of the N/10 alkali corresponds to 0.00365 gm. of HCl, the number of cc. of alkali used, multiplied by 0.0365 (if 10 cc. of gastric contents have been used) gives the percentage of total acidity, expressed in terms of hydrochloric acid. Another form of expression is sometimes used, i. e., the number of cc. of N/10 caustic soda solution required to neutralize 100 cc. of the material. This is obtained, if 10 cc. of material are used, by multiplying the number of cc. of N/10 alkali required to neutralize, by 10. The normal total acidity after a Boas meal is 0.15 to 0.30% HCl, which is equivalent to 40 to 80 cc. N/10 NaHO.

**Presence of Free Acids.**—The next step is to determine whether any of the total acidity is due to free acids, and if it is to what acid or acids. This is accomplished by the use of **indicators,** substances giving different colors with certain classes of acid or alkaline substances. The red color of alkaline phenolphthaleïn, used as an indicator above, is discharged by all four factors contributing to the acidity of the gastric contents, therefore it is used in determining the total acidity. Congo red forms an orange-yellow solution in alcohol, which, when largely diluted, is turned blue by a drop or two of a .001% solution of HCl, or by other free acids, mineral or organic, but not by acid salts. If, therefore a few drops of the gastric contents give a blue color with a drop or two of dilute congo-red solution, a free acid is present.

To detect free hydrochloric acid an indicator must be used which will react with mineral acids, but not with organic acids or with acid salts. Several have been suggested, of which the following are desirable: (1) *The phloroglucin-vanillin reaction*—Phloroglucin and vanillin are dissolved in alcohol in the proportion of 2 gm. of the

former and 1 gm. of the latter in 30 cc. of the solvent (Gunzburg's reagent). A few drops of the filtered gastric contents and the same quantity of the freshly-prepared reagent are mixed in a porcelain dish, and evaporated on the water bath: in the presence of free mineral acids a brilliant scarlet color is produced, beginning at the upper border. Delicacy=.05 p/m HCl. Not interfered with by albumoses or peptones. (2) *Resorcin-sugar*—The reagent is made by dissolving 5 gm. of resorcinol and 3 gm. of sugar in 100 cc. of dilute alcohol, and is used in the same manner as the phloroglucin-vanillin reagent, giving a rose-red color with free mineral acids. Delicacy=.05 p/m HCl. (3) *Dimethyl-amido-azobensene*—forms a yellow alcoholic solution, which turns red with free mineral acids. Delicacy=.02 p/m HCl. This and other similar tests are applied by simply mixing a few drops of the indicator with a like quantity of the contents. Papers colored with the several indicators are sometimes used, but they are not as delicate as the solutions.

Negative results of these tests with a sample of gastric contents of unknown origin do not prove that the stomach is not secreting the normal quantity of hydrochloric acid (see Quantitative, below). Such samples are met with to which double the amount of HCl normally present may be added, and not reveal its presence upon application of the tests.

**Quantitative Determination of HCl.**—Chlorin may exist in the gastric contents during digestion of usual food articles in three forms of combination: as free hydrochloric acid, as "loosely combined" acid, and as chlorids, all of which must be taken into consideration, along with the acid salts and organic acids, in determining the amount of HCl produced by the stomach. By "loosely combined HCl" is meant that portion of the free HCl secreted by the stomach which has entered into combination with the proteins to form acid-albumens; and the "effective HCl" is, clearly, the sum of the free and the loosely combined. The quantity of acid that can be thus combined is considerable. Thus 100 gm. of each of the following food articles can take up the amounts of HCl stated, in grams: Cheese –1.3 to 2.6, meat –1.6 to 2.2, milk –0.42, bread –0.3 to 0.7, beer –0.15.

Of the several methods which have been devised, probably the most desirable are those of Töpfer and of Martius and Lüttke, somewhat modified, the former, based upon the use of indicators, being the more rapid of the two, the latter, based upon chlorin determinations in part, the more accurate.

*Töpfer's Method.*—Three samples of 10 cc. each are separately titrated with N/10 NaHO solution; in (1) using phenolphthaleïn as an indicator, and carrying the addition of alkali to a distinct red, not

to faint pink as is usual. This gives the total acidity (A), made up of free HCl (L), protein HCl (C), and organic acids and salts (O). In (2) alizarin is used as an indicator, to pure violet. This gives the acidity due to (L+O), and, therefore the result of (2), subtracted from that of (1), leaves the value of (C)=protein HCl. In the third sample (3) dimethyl-amido-azobenzene is used as an indicator, to red. This gives the value of (L) alone, i. e., free hydrochloric acid. If the value of (O) be desired, it may be obtained by subtracting the result of (3) from that of (2). In each of the above titrations the number of cc. of alkaline solution used, multiplied by 0.0365, gives the result, expressed in percentage of HCl.

*Martius and Luttke's Method.*— Four samples of 10 cc. each of the filtered material are taken. In (1), the total chlorin (T) is determined either volumetrically with a N/10 solution of $AgNO_3$ and thiocyanate as an indicator, or, preferably, gravimetrically, by the usual methods. The result, expressed in terms of HCl=(T), consists of free HCl (L), protein HCl (C), and chlorin in chlorids (F). In the second 10 cc. (2), the chlorids (F) are determined by evaporating to dryness, incinerating at dull redness, redissolving in water, and determination of HCl as in (1). The effective HCl (L+C) is determined by subtracting (F) from (T). In the third sample (3), the total acidity (A) is determined by titration with N/10 NaHO solution and phenolphthaleïn. The acidity due to organic acids (O) is arrived at by subtracting (L+C) from (A). In the fourth sample (4) the free HCl (L) is directly determined by titration with N/10 NaHO, using dimethyl-amido-azobenzene as the indicator. Finally, the value of (C) is obtained by subtracting (L) from (L+C).

**Lactic Acid.**—The presence of lactic acid is detected by: (1) *Uffelmann's reagent*, which consists of a solution of $Fe_2Cl_6$ and phenol, diluted to an amethyst-blue color, which is changed to yellow by lactic acid. In order to avoid error by the action of other substances which have a like action upon the reagent, 10 cc. of the filtered gastric contents are agitated with ether, and the ethereal extract separated and agitated with the reagent; or it may be evaporated, the residue dissolved in water, and the solution added to the reagent. (2) *Boas' method*, which is more reliable, and which depends upon the formation of aldehyde from lactic acid by the action of oxidants (p. 292), and the behavior of aldehyde with Nessler's solution (p. 105). Ten cc. of the contents are treated with excess of $BaCO_3$, and evaporated to dryness on the water bath, to a syrup; this is treated with dilute $H_3PO_4$, heated to boiling, cooled, and extracted with ether by agitation. The separated ethereal extract is evaporated and the residue extracted with water. The aqueous solution is then mixed with 5 cc. $H_2SO_4$ and a little $MnO_2$, and distilled, the distillate

being received in a cylinder containing Nessler's reagent, which is turned yellow, or deposits a yellow-red precipitate, if aldehyde be present. Or the distillate may be received in a N/10 normal solution of iodin, with which aldehyde forms iodoform, recognizable by its odor, or by the formation of a yellow, crystalline precipitate, if the quantity be sufficient.

If the iodin solution be used, the process may be made a quantitative one by determining the amount of unused iodin by titration with N/10 sodium arsenite solution.

The presence of **butyric acid** may be recognized by extracting 10 cc. with 50 cc. of ether by agitation, evaporating spontaneously, and adding a few drops of water and some solid $CaCl_2$ to the solution, when oily drops separate, and the characteristic odor of butyric acid is developed. The quantity of volatile acids, butyric and acetic, may be ascertained by determining the total acidity in one sample of 10 cc. by the method given above; evaporating another sample of 10 cc. to a syrup, redissolving in water, and determining the acidity of the solution. The difference between the two determinations is the acidity due to volatile acids.

**Pepsin and Pepsinogen.**—If free HCl be present the gastric contents are examined for the presence of pepsin by placing about .05 gm. of coagulated white of egg, cut into discs or cubes, in 25 cc. of the material, which is then kept at 38-40°. Digestion should be complete in about three hours, or the edges of the fragments rounded perceptibly in less time. If no free HCl be present, pepsinogen is tested for as above, five drops of dilute HCl having been added to the material. Should the result be negative, 200 cc. of N/10 HCl should be introduced into the stomach, the contents of which are removed in half an hour and tested as above.

No quantitative method of determining pepsin is possible at present. Comparisons of the degrees of activity of a given sample of gastric contents with some pharmaceutical pepsin may be made by adding 5 cc. of the former and 0.5 gm. of the latter in two tubes to 10 cc. of a 1% solution of serum albumin containing 3 p/m of HCl, and after 24 hours determining the amount of albumin remaining undigested, by the usual methods (p. 601).

The presence of **chymosin** is tested for by keeping a mixture of 5 drops of gastric contents, and 10 cc. of milk at 38–40° for 15 minutes. If the milk be not curdled in that time, the zymogen is tested for by repeating the experiment with a mixture of 10 cc. of gastric contents, 10 cc. of milk, and 3 cc. of a 1% solution of $CaCl_2$.

Sometimes it is desirable to test the stomach contents for the **products of digestion.** This is done as follows: The filtered contents are accurately neutralized with dilute NaHO, using litmus as an

indicator; if **syntonin** be present, it will form a precipitate, soluble in excess of acid or of alkali. The liquid, freed from syntonin, is acidulated with very dilute acetic acid, and an equal volume of saturated NaCl solution is added, and the mixture heated to boiling; a coagulation indicates the presence of **native albumens.** A part of the filtrate is tested for **primary albumoses** by addition of $HNO_3$ and heating; a precipitate in the cold, which disappears with heat, and returns on cooling, indicates their presence. Another portion of the filtrate is tested for **secondary albumoses,** which are precipitated, if not present in too small amount, by saturation with NaCl. The remainder of the filtrate is saturated with $(NH_4)_2SO_4$, filtered, treated with concentrated NaHO solution in slight excess, allowed to settle, decanted, and the clear liquid tested for **peptones** with a few drops of a 2% $CuSO_4$ solution, which gives a rose-red or reddish-violet color in the alkaline solution if they are present.

**Ewald's test** for the activity of the **motor function** of the stomach depends upon the fact that salol passes through the stomach unchanged, but is decomposed in the intestine, with liberation of salicylic acid, whose presence in the urine may be then detected. About 0.7 gm. of salol are administered by the mouth, and the urine is collected at regular intervals, and tested by addition of a few drops of $Fe_2Cl_6$ solution, which gives a violet color with salicylic acid. The reaction should appear in 40 to 70 minutes, and should cease in 30 hours. The **resorptive activity** of the stomach may be tested by administering 0.2 gm. of potassium iodid in a capsule, and testing the saliva every two minutes by moistening a test-paper, made by impregnating filter-paper with starch paste, with the saliva, and then touching it with a glass rod dipped in yellow $HNO_3$, which turns blue with KI. The reaction should be obtained in 5-10 minutes.

## THE BILE.

The bile contained in the gall-bladder was early the subject of chemical investigation. It may be obtained from living animals by temporary biliary fistulæ.

The secretion of bile is continuous, but the quantity produced varies greatly at different times and in different individuals. In the dog the daily production has been found to vary from 2.9 to 36.4 grams per kilo of body-weight. No data are available to show the amount produced in 24 hours by the human subject, although it has been estimated at 500 to 950 grams, and also at 14 gm. per kilo of body-weight.

The secretion of the liver cells is thinner, clearer, and of lower sp. gr. than the bile in the gall-bladder, where the secretion of the

liver becomes mixed with the mucus of the gall-bladder. The bile contained in the gall-bladder is cloudy, somewhat viscid, alkaline; sp. gr. 1,010 to 1,040; bitter in taste, having a faint, musky odor, particularly perceptible when it is heated, and varying in color from a bright golden-yellow to a dark olive-green. In man it is usually yellow, but sometimes green.

**Composition.**—Several analyses of specimens of human bile taken shortly after death, or from biliary fistulæ, have been made, in which the numerical results have varied within tolerably wide limits. The proportions of solids and water have been found to be 89.2 to 177.3 of the former, 910.8 to 822.7 of the latter. The solids consist of mineral salts, less than 1%, "mucin" 1.3 to 3%, biliary salts 5.6 to 10.8%, cholesterol 0.16 to 0.35%, fats 0.04 to 0.9%, soaps 0.6 to 1.6%, and bile pigments, lecithins and urea. The mineral salts consist of the chlorids or phosphates of Na, K, Ca, Mg, and Fe. Copper is always present in the liver, zinc frequently, and both may be found in the bile. The mucin is partly a true mucin (a glycoproteid) and partly a nucleoalbumen. Urea is present in small amount only, but is found in large quantity in the bile of the shark.

**Biliary Salts.**—The bile of all animals contains the sodium salts of acids peculiar to this secretion. They vary in composition in different animals, but may be classed in two groups, the members of one of which (glycocholic series) yield glycocoll, or amido-acetic acid (p. 363) when boiled with acids, while those of the other (taurocholic series) yield taurin, or amido-isethionic acid (p. 366) under like treatment. The other product of the decomposition is, in both cases, **cholic acid**, $C_{24}H_{40}O_5$, whose constitution is undetermined beyond the fact that its molecule contains one CHOH group, two $CH_2OH$ groups and one COOH group. It crystallizes in octahedra or in rhombic prisms, is easily soluble in alcohol, requires 4,000 parts of cold, or 750 of hot water for its solution, is insoluble in ether, and becomes cloudy on exposure to air. In alcoholic solution it is dextrogyrous, $[a]_D = +35°$. Its Na and K salts are readily soluble in water; and their solutions are precipitated by lead acetate, or by barium chlorid. Cholic acid is easily oxidized or reduced. On oxidation it first loses $H_6$ to form **dehydrocholic acid**, $C_{24}H_{34}O_5$, a crystalline, monobasic acid, sparingly soluble, which does not respond to the Pettenkofer reaction. This then takes up oxygen to form **bilianic acid**, $C_{24}H_{34}O_8$; and this is then converted into a mixture of **cholesteric acid**, $C_{12}H_{16}O_7$, and **pyrocholesteric acid**, $C_{12}H_{16}O_5$ (p. 529). By reduction, it yields, first, **deoxycholic acid**, $C_{24}H_{40}O_4$, which also exists in putrid bile; and then **cholylic acid**, $C_{24}H_{40}O_2$. Two other acids, related to cholic acid, have been derived from human bile, one **choleic acid**, $C_{24}H_{40}O_4$, possibly identical with deoxycholic acid; the other

**fellic acid**, $C_{23}H_{40}O_4$. By boiling with acids, and during intestinal fermentation, cholic acid loses $H_2O$ and is converted into an anhydrid, **dyslysin**, $C_{24}H_{36}O_3$, which is amorphous, and insoluble in water and in alkalies.

Cholic acid and the conjugate acids containing it give the **Pettenkofer, or furfurol, reaction**: on addition of a few drops of cane sugar solution and then of concentrated $H_2SO_4$, the temperature being kept down to about 70°, the solution becomes turbid, and soon assumes a fine purple color. The colored liquid, sufficiently diluted with acid, gives a spectrum of two bands, one at F, the other between D and E, near to E. With $H_2SO_4$ alone at the ordinary temperature, solutions of the biliary acids are colored reddish-yellow, with a green fluorescence.

**Glycocholic Acid**—$C_{26}H_{43}NO_6$—predominates, in its sodium salt, in human bile and in that of the ox, but is absent in that of the carnivora. It crystallizes in silky needles, soluble in 300 parts of cold, and 120 parts of hot water, easily soluble in alcohol, insoluble in ether, which precipitates it from its alcoholic solution. Its taste is at the same time bitter and sweet. In alcoholic solution it is dextrogyrous $[a]_D = +29°$. Its Na salt is much more soluble in water than the free acid, and its solutions are precipitated by $(C_2H_3O_2)_2Pb$, $CuSO_4$, $Fe_2Cl_6$, or $AgNO_3$. When heated with alkalies or dilute acids, glycocholic acid is decomposed into cholic acid and glycocoll, $C_{26}H_{43}NO_6 + H_2O = C_{24}H_{40}O_5 + CH_2(NH_2).COOH$. Heated with concentrated $H_2SO_4$ it loses water to form **cholonic acid**, $C_{26}H_{41}NO_5$.

**Taurocholic acid**—$C_{26}H_{45}NSO_7$—exists, as its sodium salt, in human bile and in that of the carnivora, in much less amount in that of the herbivora. It is very soluble in water and in alcohol, insoluble in ether. It crystallizes with difficulty in silky needles by precipitation of its solution in absolute alcohol by anhydrous ether. These crystals rapidly deliquesce to an amorphous, resinous mass on exposure to air. Its taste is bitter and sweet. In alcoholic solution it is lævogyrous, $[a]_D = -24.5°$. Its sodium salt is very soluble, and its solutions are not precipitated by the salts which precipitate with glycocholic acid, but it is precipitated by basic lead acetate. Heated with alkalies or dilute acids, or even on evaporation of its aqueous solution, taurocholic acid is decomposed into cholic acid and taurin: $C_{26}H_{45}NSO_7 + H_2O = C_{24}H_{40}O_5 + CH_2(NH_2).CH_2.SO_3H$. Solutions of taurocholates and of glycocholates dissolve cholesterol and alkaloids, if the salt be in excess. They emulsify oils.

**Biliary Pigments**—The bile of all animals contains peculiar pigments, which are derivatives of the blood-coloring matter. The most important are **bilirubin** and **biliverdin**.

**Bilirubin**—$C_{16}H_{18}N_2O_3$—occurs in the bile of all vertebrates, par-

ticularly in that of the herbiyora, in the intestinal contents, in biliary calculi, and, pathologically, in the urine, blood, and tissues, and, crystallized as "hæmatoidin," in old extravasations of blood. It forms either an amorphous, reddish-yellow powder, or scarlet crystals, or, when crystallized by spontaneous evaporation of its chloroform solution, reddish-yellow rhombic plates. It is insoluble in water, sparingly soluble in alcohol or in ether, readily soluble in chloroform, carbon disulfid, benzene, and in alkaline solutions, with the last named of which it forms soluble compounds. It has great pigmentary power, but its solutions give no spectrum. If, however, its alkaline solutions be treated with ammonia in excess and zinc chlorid, they change in color to deep orange and then to green, and then give a spectrum of a single band near C, and between C and D. By the action of sodium amalgam upon a solution of bilirubin in weak alkali the liquid becomes opaque, and, after two or three days, turns brown, when upon addition of HCl, it turns red and deposits brown flocculi of a substance which closely resembles, if it is not identical with, the stercobilin of the fæces and the urobilin of the urine. This substance, which is called hydrobilirubin, $C_{32}H_{40}N_4O_7$, is formed from bilirubin by hydrogenation, followed by oxidation of its solution in air: $2C_{16}H_{18}N_2O_3+3H_2+O_2=C_{32}H_{40}N_4O_7+H_2O$. Solutions of bilirubin on exposure to air soon become green from formation of biliverdin by oxidation.

The reactions of bilirubin are utilized for the detection of bile in the urine and elsewhere. They are: (1) *Gmelin's reaction* — The liquid examined is floated upon the surface of nitric acid containing a little nitrous acid, when a series of colors, green, blue, violet, and reddish-yellow, are produced at the union of the two layers, of which the green is the most marked. There must be no alcohol present. Limit 1:80,000. This reaction depends upon a progressive oxidation, with formation of the following products: (*a*) biliverdin; (*b*) bilicyanin, whose neutral solutions are of a fine blue color, with red fluorescence, and whose alkaline solutions are green, and give a spectrum of three bands, one between C and D, nearer to C, one over D, and the third near to E, between E and F; (*c*) a red pigment, the nature of which has not been determined; (*d*) choletelin, a brownish-yellow pigment, whose alcoholic solution gives a spectrum of one band between E and F.. (2) *Hammarsten's reaction*—The reagent used is made by mixing 1 vol. $HNO_3$ with 19 vols. HCl, and letting the mixture stand until it is yellow. A colorless liquid is formed by mixing 1 vol. of this reagent with 4 vols. of alcohol, which is colored intensely green by a trace of bilirubin. (3) *Huppert's reaction*—The liquid is treated with calcium chlorid and ammonia; and the precipitate formed is washed with water, and covered while still moist in a

test-tube with alcohol and acidulated with hydrochloric acid, which is then heated to boiling. In presence of bilirubin the liquid becomes emerald-green.

**Biliverdin** — $C_{16}H_{18}N_2O_4$ — accompanies bilirubin, and is most abundant in green biles. It is amorphous, insoluble in water, ether or chloroform, soluble with a green color in alcohol and in glacial acetic acid, or with a brown color in alkalies. It is precipitated from its solutions by acids and by salts of Ca, Ba, and Pb. It responds to the tests for bilirubin. Reducing agents convert it into bilirubin; oxidizing agents into **biliverdic acid**, $C_8H_9NO_4$. It is best obtained by oxidizing bilirubin.

**Bilifuscin** is a brown, amorphous pigment, occurring in biliary calculi and in putrid bile, which is soluble in alcohol and in alkalies, insoluble in water, ether or chloroform. It does not respond to the Gmelin reaction. **Biliprasin** is the name given to a green pigment occurring in biliary calculi, which is probably a mixture or combination of bilirubin and biliverdin. **Bilihumin** is a brown, amorphous pigment, obtained from biliary calculi, which is insoluble in alcohol, ether or chloroform, and which does not give the Gmelin reaction.

**Cholesterol — Cholesterin** — $C_{27}H_{43}OH$ — is a monoatomic alcohol of unknown constitution, which exists normally in almost every animal tissue and fluid, in many in very minute quantity, most abundantly in the bile, nerve tissues, intestinal contents, fæces, and in sebum and wool-fat. In pathological products it is frequently an abundant constituent, and is met with in biliary calculi, certain brain tumors, atheromatous degenerations, pus, the fluids of cysts, hydrocele, etc., as well as in cancerous and tubercular deposits, and in the lens in cataract. In some of these situations it exists free, in its peculiar, crystalline form of very thin, colorless, rhombic plates, while in others it is in combination in the form of its esters. It also exists in the vegetable world, widely distributed, notably in peas, beans, olive-oil, wheat, etc.

Cholesterol is insoluble in water, in alkalies, or in dilute acids, difficultly soluble in cold alcohol, readily soluble in hot alcohol, ether, benzene, acetic acid, glycerol, and solutions of the biliary acids. It is odorless and tasteless; f. p. 145° (293° F.); sp. gr. 1.046. It is laevogyrous, $[a]_D = -31.6°$, in any solvent. It combines readily with volatile fatty acids, and from its solution in glacial acetic acid a compound, $C_{27}H_{43}O.C_2H_3O_2$, crystallizes in fine curved needles, which are decomposed on contact with water or alcohol. When heated with acids under pressure, it forms true esters, some of which also exist in wool-fat, and in "lanolin," derived therefrom. By oxidation it yields a series of acids, from **cholesteric acid**, $C_{26}H_{42}O_4$—

not identical with the acid of the same name derived from cholic acid (p. 526)—to **trioxycholesteric acid**, $C_{26}H_{42}O_7$.

Cholesterol may be recognized by the following characters: (1) Its crystalline form, thin rhombic plates, usually having one obtuse angle missing. (2) If these crystals be moistened with dilute $H_2SO_4$ (1:5) they are colored, first bright carmine, and then violet, beginning at the borders. If iodin solution be now added, the color changes to bluish-green, then to blue. (3) When $H_2SO_4$ is added to a solution of cholesterol in chloroform, the liquid is colored purple, changing during evaporation to blue, green and yellow (Salkowski). (4) If acetic anhydrid be added to a chloroform solution of cholesterol, and then a drop or two of concentrated $H_2SO_4$, the mixture becomes first red, then blue, and finally green (Liebermann-Burchard). (5) When a mixture of 2–3 vols. of $H_2SO_4$ or HCl and one vol. of dilute $Fe_2Cl_6$ solution is evaporated upon cholesterol, a residue is obtained which is at first purple, then violet (Schiff). (6) When moistened with concentrated $HNO_3$ and the liquid evaporated, cholesterol leaves a yellow residue, which is colored dark orange-red by $NH_4HO$ or NaHO (see Murexid Reaction, p. 355). (7) Pure, dry cholesterol, moistened with propionic anhydrid and dried and fused, leaves a residue which on cooling becomes first violet, then blue, green, orange, carmine-red, and finally copper-colored (Obermüller).

**Isocholesterol** has the formula $C_{26}H_{43}OH$, formerly assigned to cholesterol. It occurs in wool-fat, accompanying cholesterol, from which it differs in its f. p. $=138°$ (280.4° F.), and in not responding to the Salkowski reaction.

**Origin and Destiny of the Biliary Constituents.**—The **biliary salts** are produced in the liver, and do not preëxist in the blood. This is proven by the facts that they do not accumulate in the blood after extirpation of the liver in frogs, and that in dogs they are absorbed by the lymphatics of the liver and carried to the blood by the thoracic duct after ligation of the ductus choledochus, but they do not appear in the blood after ligation of both ductus choledochus and thoracic duct. Although the immediate antecedents of the biliary salts are not known, they are probably formed by union of their constituents, which are derived from different sources. Cholic acid, containing neither nitrogen nor sulfur, and containing both alcoholic and carboxyl groups, is in all probability derived from a carbohydrate, or possibly from the fats. Glycocoll and taurin both contain nitrogen, and the latter sulfur also. They are, consequently, derived from the proteins. Glycocoll is one of the principal products of decomposition of collagen and other albuminoids, although it has not been obtained from the true albumens (p. 508). The biliary salts are not reabsorbed unchanged from the intestine under normal

circumstances, or, at all events, not in any notable quantity. Solutions of these salts, when injected into the circulation, are rather active poisons. In small doses they cause diminution in the frequency of the pulse and of the respiratory movements, lowering of the temperature and arterial tension, and disintegration of the blood-corpuscles. In large doses (2–4 gm. to a dog), they produce the same effects to a more marked degree, and, further, epileptiform convulsions, black and bloody urine, and death. These effects do not follow the injection of the products of decomposition of the biliary acids, except cholic acid, and with that the symptoms are much less marked. Nor are the biliary salts found as such in the fæces, except that these occasionally contain glycocholic acid, but never taurocholic acid, which is more readily decomposed. Sometimes cholic acid or, more frequently, dyslysin occurs in the fæces, but not glycocoll or taurin. The decomposition of the biliary salts which occurs in the intestine is due to fermentative (bacterial) action, as the contents of the lower intestine in the fœtus contain notable quantities of biliary salts. That the taurin resulting from the decomposition is reabsorbed is demonstrated by the fact that it appears in the urine, partly in its own form and partly as taurocarbamic acid, formed by the union of taurin and carbamic acid: $C_2H_7NSO_3 + CO_2NH_3 = C_3H_8N_2SO_4 + H_2O$. Equally direct proof of the reabsorption of glycocoll is not at hand; but the ready formation of uric acid (p. 358) and of hippuric acid (p. 425) from glycocoll render it probable that the latter substance is an intermediate product in the formation of the other two, in part at least, in the economy.

The **biliary pigments** are also formed in the liver, and do not preëxist in the blood, although bilirubin at least may be formed in other parts of the body, and has been found in old extravasations of blood, and in the placenta. The formation of these pigments in the liver is proven by the following facts: in pigeons, the biliary pigments make their appearance in the blood in five hours after ligation of the bile-ducts; but if the blood-vessels of the liver are ligated at the same time, no pigments appear in the blood or tissues in 24 hours. In geese, poisoned with hydrogen arsenid, the biliary pigments appear in the urine in large quantity; but if the liver have been extirpated before the poisoning this does not occur.

The parent substance of the biliary pigments is undoubtedly the blood coloring matter. The chemical relationship between bilirubin and certain derivatives of hæmoglobin is very close. Indeed bilirubin is identical with hæmatoidin, which is found in old blood stains, and, in the crystalline form, in old extravasations of blood. Bilirubin is also isomeric with hæmatoporphyrin, a pigment normally present in the urine in small amount, and notably increased therein in poisoning

by sulfonal. The relation between hæmatin and bilirubin is shown by the equation: $C_{32}H_{32}N_4FeO_4+2H_2O=2C_{16}H_{18}N_2O_3+Fe$, which may, in some modified form, indicate the method of formation of the biliary pigment. The iron thus liberated has been accounted for only in part. The bile always contains iron, principally in the form of ferric phosphate, to the proportion of from 0.04 to 0.115 p/m. But the correspondence between the amount of iron present and the amount of bilirubin formed, which the above equation would call for, has not been found to exist. For 100 parts of bilirubin present in the bile, 1.4 to 1.5 parts of iron have been found, whereas an equivalent quantity of hæmatin would yield 9 parts. Moreover, in poisoning by hydrogen arsenid, in which there is an increased formation of bile pigment, no corresponding increase in the amount of iron in the bile has been observed. Probably a large portion of the iron enters into some form of combination as a protein or pigment, from which the bilirubin is subsequently derived.

There is no correspondence in the observed variations in the quantities of biliary salts, and of biliary pigments formed. As these variations take place independently of each other, the processes of formation of the two classes of substances may be considered as being distinct from each other.

The biliary pigments are not reabsorbed unchanged in health. When they are pathologically (icterus, phosphorus poisoning) they stain the skin and tissues, and make their appearance in the urine. The coloring matter of the fæces, stercobilin, and at least one of those of the urine, urobilin, are derived from bilirubin (p. 592).

Cholesterol exists in the protoplasm of all cells, and is particularly abundant in nerve tissues. In analyses of brain substance it has been found to constitute a large portion of the solid constituents of both white and gray matter, particularly of the former. It is constantly present in the fæces in its own form or in that of a derivative (koprosterin, stercorin), and only appears in the urine in chyluria. It is, in all probability, a product of dissassimilation, produced principally in nervous tissues.

Biliary Calculi.—Calculi are frequently met with in the gall bladder after death, and the smaller ones often pass into the intestine during life. These calculi may be divided into three classes, according to the nature of their chief constituents: (1) *Pigmentary calculi*, consisting chiefly of the several pigments mentioned above, combined with calcium, and sometimes associated with calcium salts. They are usually multiple, sometimes very numerous. They are yellow, green, brown or black in color; sometimes rounded and nodulated upon their surfaces, more usually having flattened surfaces, and more or less perfect geometrical shapes, produced by attrition one against the

other. In cattle these stones are sometimes found as large as a walnut. (2) *Cholesterol calculi*, consisting almost entirely of cholesterol. They are usually single, rounded and polished, having a nacreous appearance and an ovoid outline. They may measure nearly an inch in their longer diameter. (3) *Calcic calculi* are much more rare in the human subject than the other two forms. They consist mainly of tricalcic phosphate and calcium carbonate.

## PANCREATIC SECRETION.

The secretion of the pancreas can be obtained from temporary fistulæ in animals, or permanent fistulæ may also be established, but the secretion obtained from the latter generally becomes changed from the normal in composition in a few hours. Its secretion is normally continuous in the herbivora, but interrupted in the carnivora, and in the herbivora during starvation. The maximum of secretion is reached in about three hours after eating, with another rise from two to four hours later. In dogs the amount secreted is estimated at 22 cc. per kilo. of body weight. The pancreatic juice of the dog is clear, colorless, odorless, slightly viscid, sp. gr. 1008 to 1010, and strongly alkaline, the alkalinity being equal to about 3 p/m of $Na_2CO_3$.

**Composition.**—The secretion from a temporary fistula in the dog contains: water, 900.8; solids, 99.2. The solids consist of mineral substances 8.8, and organic substances 90.4. The pancreatic secretion found in an occluded canal of Wirsung, in a man suffering from cancer, contained a much smaller quantity of solids: 24.1 p/m, of which 11.5 p/m consisted of peptones and enzymes, and 6.2 p/m of salts (Herter).

The mineral constituents are sodium and potassium chlorids and phosphates, sodium and potassium carbonates, to which the liquid owes its alkalinity, and compounds of calcium, magnesium and iron. The organic constituents include a little leucin, fat, and soap, much albumen, sufficient to cause the liquid to form a solid coagulum when it is heated, and at least three enzymes, one a proteolytic enzym, **trypsin**, another an amylolytic enzym, **pancreatic diastase**, and the third having a saponifying action, **steapsin.**

**Trypsin.**—This enzym does not exist in the gland, which contains a zymogen, from which the enzym is produced by the action of water, acids, alcohols, etc. The product most nearly approaching purity is probably that obtained by Kühne's method, which consists essentially of precipitation by alcohol and subsequent purification. It is very soluble in water, insoluble in alcohol or in glycerol, although if less pure it dissolves in glycerol, which may be used to obtain

an active extract of the pancreas. In aqueous solution it is decomposed into a coagulated albumen and peptone by addition of a little acid and boiling. The relatively pure enzym is destroyed in five minutes in solution containing 0.5% $NaHO$, at 50°. In neutral solution it is destroyed at 45°, less rapidly in presence of albumoses. The characteristic property of trypsin is its power of dissolving coagulated proteins in alkaline or in extremely faintly acid solution. Its action upon fibrin is the most energetic, but it also dissolves coagulated albumins and globulins rapidly, and gelatin, which is not dissolved by pepsin, as well. It acts best in the presence of 3 to 4 p/m of $Na_2CO_3$. Its action is arrested by the presence of even very small quantities of mineral acids, but not by protein-hydrochloric acid (p. 522). Organic acids cause less interference, and lactic acid in the proportion of 0.2 p/m in presence of bile and NaCl, none whatever. Its action is diminished by accumulation of its products. It is very prone to putrefaction. Trypsin is more active and causes greater changes than pepsin. As indicated above (p. 519), it decomposes the amphopeptone of peptic digestion into anti-peptone and hemi-peptone. Independently of peptic action, and if putrefaction be prevented by operating in liquids containing a little thymol or chloroform, it produces from albumin or fibrin albumoses, peptones, leucin, tyrosin, aspartic acid, and even lysin, lysatinin, arginin and histidin (p. 499). During the action of trypsin upon albumin a substance called proteinochromogen, or tryptophan, is also produced. This body produces, with chlorin or bromin, a reddish-violet derivative, proteinochrom, which is very unstable and highly diffusible. The bromin derivative is, apparently, related to hæmatoprophyrin and to bilirubin.

Trypsin in alkaline solution coagulates milk, decomposes the nucleins, pseudonucleins, glycoproteids and hæmoglobins, with solution of the albumens liberated, and converts gelatin into gelatopeptones. Collagen is not affected, unless previously acted upon by acids (p. 508). It does not act upon keratin or upon chitin.

Pancreatic diastase, also called amylopsin, does not exist in the pancreatic secretion of infants, and only makes its appearance after the first month of life. It is very similar to ptyalin, but probably not identical with that enzym. Its action upon cooked starch is very energetic, and it also decomposes raw starch more slowly at 37° to 40°. The products of its action upon starch are dextrin, isomaltose and maltose, with very little glucose.

Steapsin is the saponifying enzym of the pancreatic secretion. It decomposes the neutral fats into glycerol and fatty acid, the latter combining with the alkalies present to form soaps. It is thus also, indirectly, an emulsifying agent.

## INTESTINAL SECRETIONS.

The "**intestinal juice,**" *succus entericus*, is the product of a great number of small glands, including Brunner's glands, Lieberkühn's follicles, Peyer's patches and the solitary glands. Its study is attended with great difficulty, not only because it can only be obtained from portions of the intestine, by isolating a portion of the gut in animals, or by the occurrence of artificial anus in the human subject, but also because of the difficulty in determining what portion of the observed actions are due to the secretion of these glands and what to bacterial action, etc. About all known concerning it is that it has an alkaline reaction equivalent to 4 to 5 p/m of $Na_2CO_3$; that it contains albumin, albumoses and a mucin; that it does not act upon the proteins, has but a slight action upon cooked starch, and does not saponify fats. Its most prominent action, supposed to be caused by an enzym, **invertin**, is that of inverting the disaccharids, saccharose, maltose and lactose (p. 270). It also aids in the emulsification of the fats, in presence of proteins and of an alkaline reaction.

## CHEMICAL CHANGES OCCURRING IN THE INTESTINE.

The changes which the constituents of the food undergo in the alimentary canal are the sum of the effects produced by the several digestive secretions, modified by their influences upon each other's actions, and the chemical reactions set up by bacterial life, constantly present and active. The changes in the organic food-constituents, carbohydrate, fatty and protein, are briefly the following:

**Carbohydrates.**—The amylolytic action of the ptyalin of the saliva upon hydrated starch is arrested by the acid reaction of the gastric contents, but may continue for some little time in the stomach in the interior of difficultly permeable masses of starchy foods, particularly as a certain degree of acidity is required to arrest the action. But once arrested, it is not reëstablished, so far as salivary action is concerned, when the reaction returns to alkaline in the intestine. In the intestine the powerful diastatic action of the pancreatic enzym, favored by the presence of the bile, takes the place of salivary action and continues the amylolytic hydrolysis to the formation of disaccharids. Inversion of the disaccharids, cane-sugar, milk-sugar, and maltose, is effected by the invertin of the intestinal secretion, and also by bacterial action. Even cellulose, if finely divided, is to some extent converted into soluble derivatives in the intestine, but by what agency is unknown.

**Fats.**—The known chemical change which the fats undergo during

digestion is limited to a not very abundant saponification, caused by the pancreatic enzym. The liberated fatty acids combine in part with the alkali of the bile and of the pancreatic juice to form soaps, which favor the conversion of the remainder of the fats into the form of emulsion in which they are absorbed by the lacteals.

**Proteins.**—The chyme, more or less strongly acid in reaction, and rich in albumoses and ampho-peptones, the products of peptic digestion, is greatly modified shortly after its passage into the duodenum, where an entirely different series of processes are begun. The albumens and acid albumens of the gastric contents are precipi-ted by the bile in acid, not in alkaline reaction, that is by the free ary acids, and notably by taurocholic acid, but not by the biliary ts. Peptones are not so precipitated. But the protein precipitate med by the bile is redissolved by an excess. It is doubtful nether this precipitation occurs to any considerable extent in the human subject, in whom the alkalinity of the bile and pancreatic retion, discharged into the intestine by a common opening, soon overcomes the acidity of the chyme. So soon as the reaction passes m acid to alkaline, peptic digestion ceases, and the more energetic tryptic digestion takes its place, causing the reduction of the albumoses and ampho-peptones to simpler forms of combination. Here also fermentative, or bacterial, changes begin, to continue throughout the intestinal tract. As a result of bacterial action upon the carbohydrates, lactic acid and acids of the acetic series are produced, which, in their turn, gradually overcome the alkalinity caused by the bile and pancreatic secretion, until, in the lower ileum, the reaction again becomes acid, to continue so throughout the remainder of the intestine. But the acids here generated are not such as interfere with tryptic digestion, in the amounts in which they are formed (p. 534). Bacterial action is most intense in the upper part of the large intestine, and diminishes as water is removed by absorption. The products of intestinal putrefaction (for the process is very similar to anærobic putrefaction outside the body) are: albumoses, peptones, amido-acids, ammonia, indole, skatole, phenol, paracresol, phenylic acids, volatile fatty acids, mercaptan, hydrogen sulfid, carbon dioxid, methane, and hydrogen. These are partly discharged with the fæces and intestinal gases, but are also in large part reabsorbed. Several reappear in the urine in forms modified by oxidation, or by synthetic processes. Indole, skatole, and phenol, for example, exist in synthetic derivatives in the urine, and the amount of the indole derivative, indican, eliminated by the urine, is an index of the extent of reabsorption of the products of intestinal bacterial action occurring at the time. Certain constituents of the digestive secretions are themselves modified by bacterial action. Thus the biliary pigments

are converted into stercobilin or urobilin, and the biliary acids are split into their factors.

The intensity of bacterial action is held in check by three agencies: by the removal of water and of the products of digestion by absorption, by the antiseptic action of the biliary acids, and by the increase in the amount of lactic acid. Taurocholic acid prevents putrefaction and fermentation when present in the proportion of 0.2% to 0.5%. Glycocholic acid is much less active in this respect.

**Intestinal Gases.**—The gases of the intestine consist largely of nitrogen, derived from swallowed air. Oxygen exists only in very small amount, having been absorbed either by the host or by the bacteria. Carbon dioxid is constantly present in notable amount, produced by putrefaction of the proteins, by fermentative decomposition of the carbohydrates, and by neutralization of the sodium carbonate of the bile and pancreatic juice. Hydrogen is formed by bacterial growth. Minute quantities of hydrogen sulfid, resulting from decomposition of the proteins; and of methane, from decomposition of both proteins and carbohydrates, are also present.

**Fæces.**—All substances taken into the mouth, which are not either dissolved and absorbed, or vomited, must appear in the fæces. These are, therefore, the more abundant the greater the amount of indigestible material, cellulose, keratin, etc., contained in the food. The fæces may also contain slowly digestible material, shreds of muscular tissue, starch, coagulated casein, fat, which have escaped digestion by a too rapid passage through the alimentary canal, or from having been taken in excessive amount. Besides the undigested food residues, the fæces contain substances formed in the body either by its own action or that of the fauna and flora inhabiting the alimentary canal. These consist of morphological elements derived from the mucous membranes and glands; mucins, cholesterol (excretin, stercorin), cholic acid, dyslysin, stercobilin and mineral salts derived from the bile and other secretions; indole, skatole and other products of bacterial life, and the micro-organisms themselves; sometimes, also, entozoa or their ova, pathogenic microbes, and insoluble residues of medicinal substances. The reaction of the fæces of adults is alkaline, the acidity due to the volatile fatty acids and lactic acid, produced by putrefactive changes, having been more than overcome by the alkalinity of the ammonia and amins, produced by ammoniacal fermentations. In nursing infants, in whom a considerable quantity of lactic acid is formed from the milk-sugar, the reaction is acid. The normal color of the fæces is due to stercobilin (hydrobilirubin), derived from the biliary pigments. When the bile is deficient, the fæces are pale in color, and contain a large quantity of fat. The fæces are sometimes almost black in color, either from

the presence of hæmatin or hæmatoidin after hæmorrhages, or from the presence of dark-colored metallic sulfids after administration of the salts of iron, bismuth or lead. When these sulfids are present they frequently deposit as heavy, dark-colored powders at the bottom of the vessel. The fæcal odor is largely that of indole and skatole, somewhat modified by the odors of ammonia and of hydrogen sulfid.

**Meconium** — the contents of the lower intestine of the fœtus at birth—is dark brown or green in color, almost odorless, acid in reaction, and semi-solid in consistency. It contains epithelial cells, frequently stained green, fat globules, crystals of cholesterol and of bilirubin. In chemical composition it consists of about 80% water and 20% solids. The solids consist of mucin, biliary acids and pigments, cholesterol, fat, soaps, peptones, leucin, tyrosin and salts, notably calcium and magnesium phosphates. Stains produced by meconium may be distinguished from fæcal stains by the fact that the former give Gmelin's and Pettenkofer's reactions, while the latter do not.

**Intestinal Concretions.** — Besides gall-stones, the intestine may contain true intestinal concretions, which are, however, of much rarer occurrence in the human subject than in the lower animals. They usually consist of concentric layers of calcium carbonate or of tricalcic phosphate, with a little fat and pigment, deposited upon some insoluble foreign substance as a nucleus, or they may be formed in the vermiform appendix without a nucleus. The intestines of horses and cattle frequently contain large calcic calculi, sometimes weighing several pounds (16 lbs. in a horse); or "hair-balls," consisting of masses of hair agglutinated into hard balls. **Bezoar stones** are concretions from the intestines of certain goats and antelopes, which contain either **lithofellic acid**, a peculiar acid related to cholic acid, or **ellagic acid**, a derivative of gallic acid, and biliary pigments. **Ambergris** is an intestinal concretion of the whale, containing a non-nitrogenized substance, **ambraïn**, related to cholesterol.

## THE BLOOD.

The blood being the circulating medium by which oxygen and the products of digestion are carried to the tissues, and by which the waste products of tissue metabolism are carried to the excretory organs, varies notably in composition in different parts of the circulation at different times and under varying conditions of health or disease.

The living, circulating blood consists of two parts, the **plasma**, the liquid portion, and the **corpuscular elements** suspended therein.

It is desirable to consider the chemistry of these two constituents of the blood first, and subsequently that of the blood as a whole.

The blood, very soon after being removed from the living animal, undergoes the chemical and physical change of **coagulation**, involving modification of the proteins of the plasma, and the separation of the blood into the two new divisions of **clot**, consisting of the newly-formed fibrin and the corpuscles; and the **serum**, containing those constituents of the plasma not concerned in the formation of fibrin. In order, therefore, to obtain the plasma and corpuscles free from each other some method must be adopted to prevent the occurrence of coagulation during the separation. Several methods have been used for this purpose :

(1) By taking advantage of the fact that the blood of the horse coagulates very slowly at low temperatures. Horse's blood is collected in a tall, narrow glass vessel, surrounded by a freezing mixture of ice and salt, which is then maintained at 0° until the corpuscles have settled. Coagulation does not take place for several days.

(2) On a small scale the corpuscles may be separated from the plasma by increasing the rapidity of their deposition by the use of the **hæmatocrit**. This is simply a centrifuge revolving with great rapidity (3,000 to 5,000 revolutions a minute). With the very narrow tubes used, the separation is complete in about two minutes, and before coagulation has interfered.

(3) The centrifuge, revolved at a lower speed, may be also used with larger quantities of blood, but then some agency must be used to delay coagulation. One method consists in injecting a solution of albumose into the circulation of a dog, collecting the blood and centrifugating it. The plasma so obtained is known as **peptone-plasma.** Or an infusion of the mouth of the leech may be similarly used.

(4) If the blood, as it flows from the vessel be mixed with either an equal volume of saturated solution of sodium sulfate, or with the same quantity of a 10% sodium chlorid solution, or with one-third its volume of a saturated solution of magnesium sulfate, and the mixture maintained at a low temperature, coagulation will be delayed sufficiently to permit the corpuscles to settle. This plasma is called **salt plasma.**

(5) The best method depends upon the removal of the calcium salts, whose presence is necessary to coagulation, by precipitation as calcium oxalate. The blood is received in a dilute solution of potassium oxalate in such proportion that the mixture contains 0.1% of oxalic acid, and the mixture set aside until the corpuscles deposit. The plasma, known as **oxalate plasma,** regains its power of coagulation on restoration of the calcium salts.

## PLASMA AND SERUM.

The plasma, at the temperature of 0°, above which it rapidly coagulates into clot and serum, is a viscid liquid, yellowish, or greenish-yellow in color, strongly alkaline in reaction.

**Composition.**—But few complete analyses of blood-plasma have been made. Indeed, considering the variations in its quantitative composition, above referred to, the results of such analyses can only be considered as applying to the particular sample analyzed, and not as representing the mean composition of the plasma except in a general way. The following are results obtained from horse's blood, the first an analysis by Hoppe-Seyler, the latter the mean of three analyses by Hammarsten:

| | I. | II. |
|---|---|---|
| Water | 908.4 | 917.6 |
| Solids | 91.6 | 82.4 |
| Protein bodies | 77.6 | 69.5 |
| Fibrinogen | 10.1 | 6.5 |
| Serum globulin | 67.5 | 38.4 |
| Serum albumin | | 24.6 |
| Fat | 1.2 | |
| Extractives | 4.0 | |
| Soluble salts | 6.4 | 12.9 |
| Insoluble salts | 1.7 | |

**Fibrinogen**, the parent substance of fibrin, exists in the plasma, chyle, lymph, and in transudates and exudates. It has the characteristic property of coagulating in presence of calcium salts and an enzym (thrombin), with formation of fibrin. When moist, it forms viscid, elastic masses or flocks, which readily fuse together. It has the general properties of the globulins, from which it differs in that the addition of calcium chlorid solution to its very faintly alkaline and salt-free solution causes a precipitate which contains calcium, and soon becomes insoluble. This precipitate is not formed in presence of sodium chlorid, nor with an excess of calcium chlorid. Fibrinogen is soluble in dilute sodium chlorid solution, and this solution, neutral, or very faintly alkaline, coagulates at 56°. Its solutions are precipitated by addition of an equal volume of saturated sodium chlorid solution, and, completely, by excess of the solid salt; in which latter respect it differs from serum-globulin. It decomposes hydrogen peroxid energetically. Its solutions are lævogyrous, $[a]_D = -52.2°$. It is obtained from salt- or oxalate-plasma by precipitation with an equal volume of saturated salt solution and purification.

**Fibrin** is the substance formed in the so-called spontaneous coagulation of blood, lymph, and transudates, or by the addition of serum, or of thrombin, to a solution of fibrinogen. The typical fibrin, as obtained by whipping blood with a bundle of twigs or broom, and washing until white, is in elastic fibers, insoluble in water, alcohol, or ether. In dilute salt solution, putrefaction being prevented, it dissolves very slowly at the ordinary temperature, somewhat more rapidly at 40°. In solution of HCl, KHO, or NaHO of 1 p/m it swells, gelatinizes, and slowly dissolves after some days. It decomposes hydrogen peroxid energetically, but not after having been heated, or in contact with alcohol.

A solution of pure fibrinogen does not coagulate at the ordinary temperature, but it does so very soon after addition of a little blood-serum, or of a fragment of fibrin washed with water only. These therefore contain a substance, an enzym, called **thrombin**, or **fibrin-ferment**, which sets up the conversion of fibrinogen into fibrin. This substance is by some believed to be a globulin, by others a nucleo-proteid. It is active in very small amount, most active at about 40° and in presence of calcium salts. It does not act in the absence of neutral salts, and its power is completely destroyed by a temperature of 70°. The coagulation of blood is, however, a more complex process than the coagulation of fibrinogen alone, and in it the corpuscles play a part (see below). The plasma is believed to contain, not thrombin, but its zymogen, **prothrombin**, which is converted into thrombin by the soluble calcium salts.

**Serum-globulin — Paraglobulin — Fibrinoplastic substance** — occurs in the blood-plasma and serum, and in the red and white blood-corpuscles, and constitutes more than half of the total proteins of the blood, also in lymph, in transudates and exudates, and pathologically in the urine. It is probably not a simple substance, but a mixture of two or more globulins. It has the general properties of the globulins. When moist it forms white flocks, not elastic or sticky. It differs from fibrinogen in not being precipitated by an equal volume of saturated sodium chlorid solution, and only incompletely by salting with sodium chlorid to saturation. It is completely precipitated by salting with magnesium sulfate, or by addition of an equal volume of saturated ammonium sulfate solution. Its coagulation temperature in solutions containing 5 to 10% of sodium chlorid is 75°. Its solutions are lævogyrous, $[a]_D = -47.8°$. Serum-globulin, as usually obtained from blood, when boiled with dilute acids, yields a reducing substance. A glycoproteid, or jecorin, is therefore contained in it or carried down with it.

Serum-globulin is obtained from blood-serum by slight acidulation with acetic acid, and addition of from 10 to 20 volumes of water,

when it separates as a flocculent precipitate, which is purified by solution in dilute salt solution, and reprecipitation by water. As so obtained it is not free from lecithins and thrombin. It can be obtained free from the latter from the fluid of hydrocele.

**Serum-albumin**—occurs in blood-plasma and serum, in lymph, in transudates and exudates, probably in many tissues, and, pathologically, in the urine. When moist it is a white, flocculent material; when dry, translucent, gummy, brittle, and hygroscopic. It has the general properties of the albumins. It is not a simple substance, but a mixture of three **serines**, of which one is amorphous and two crystalline, one crystallizing in hexagonal prisms, the other in long needles. The mixed serum-albumin has a coagulation temperature varying from 70° to 85°, depending upon the quantity of NaCl present, and the reaction. It is lævogyrous, $[a]_D = -62.6°$ to $64.6°$. It has not been obtained entirely free from salts. From solutions containing the minimum amount of salts it is not coagulated by heat or by alcohol, but is after addition of NaCl.

**Blood-serum.**—When blood is drawn from the blood-vessels it soon coagulates into a jelly-like mass, occupying the volume of the original liquid. This mass soon contracts and expels a liquid, which is the **serum**, and which differs from the plasma in that it contains thrombin, and has lost fibrinogen. In other respects the two are qualitatively alike. It is a sticky liquid, more strongly alkaline than the plasma, sp. gr. 1027 to 1032, pale yellow, with a greenish tinge, usually clear, but opalescent or milky during digestion of fats.

The constituents of the plasma and of the serum, other than the proteins, being identical, are most readily studied in the serum, which is more easily obtainable than the plasma. They include the fats, carbohydrates, extractives and mineral salts. The term "extractives," in an analytical statement, is the equivalent of "miscellaneous" in a classification, and the substances arranged under this head are of diverse nature, present in small quantity, and, while they are not separately determined in the particular analysis referred to, some of them are of great physiological interest.

**Fats**—exist in the plasma or serum, suspended in minute oil globules, as a fine emulsion. They are present during fasting in the proportion of 1 to 7 p/m, and are greatly increased in amount during digestion of fats. Soaps, derived from the fats, are also present. Besides the true fats (p. 318), the plasma contains lecithins (p. 319), cholesterol and cholesterol esters (p. 529).

**Carbohydrates.**—The carbohydrates of the blood appear to exist almost exclusively in the plasma, none having been found in the corpuscles, except glycogen in the leucocytes. They consist of glucose, glycogen (?), and a carbohydrate in some form of nitrogenized

or phosphorized combination. Glucose is considered to be a constant constituent of the plasma, even during starvation, and to be present in about the proportion of 1 to 1.5 p/m, without any notable variations in different parts of the circulation under normal conditions, except that it is greatly increased in amount in the portal blood during digestion of carbohydrates. The analytical results in this regard, however, require revision, in the light of the discovery in the blood of a reducing substance other than glucose (see Jecorin, p. 544). The amount of reducing substance in the blood is increased after hæmorrhage, and in diabetes. When the proportion of sugar in the blood exceeds 3 p/m (hyperglykæmia), either from excessive absorption, or, in natural or experimental diabetes, it is eliminated by the urine (glycosuria). It is doubtful whether the plasma contains glycogen, which is a constituent of tissue elements rather than of fluids in the body. That the plasma contains small quantities of a substance which does not reduce Fehling's solution, but which yields a reducing substance on boiling with dilute acids, is certain, but whether any of this is glycogen or not remains to be determined. The whole of the reducing substance so produced by acids is not derived from glycogen. A part, and possibly all, is derived from the decomposition of jecorin, or a jecorin-like substance, present in the plasma. This may also be the origin of the so-called **animal gum**, obtained from the serum, which yields a reducing substance by the action of boiling dilute acids, is said to have the formula $(C_6H_{10}O_5)_n$, does not ferment, and is optically inactive.

**Enzymes.**— The plasma contains several enzymes or zymogens, which are probably produced by the corpuscular elements: (1) **Prothrombin**, the zymogen of thrombin, the fibrin-forming enzym; (2) **a diastatic enzym.** Blood serum or lymph, added to starch paste or glycogen solution, brings about the formation of maltose and isomaltose, if the mixture be kept at about 40°; (3) **a glucase**, or inverting enzym, which causes the inversion of the product of the diastatic action, with formation of glucose, if the action above mentioned be allowed to continue; (4) **glycolyse.** The proportion of glucose in blood serum gradually diminishes on standing, even in the absence of all organized ferments. This glycolysis is due to the action of an enzym whose function is destroyed by a temperature of 54°, and which apparently originates from the leucocytes; (5) **a lipolytic enzym**, which saponifies neutral fats. Besides the above, the blood contains substances, probably enzymes, existing in or derived from the corpuscular elements, which bring about the conversion of the emulsified fats into some unknown form of soluble combination, and which arrest the action of the pepsin, trypsin and chymosin absorbed from the intestine.

Jecorin — is a substance obtained from the liver, spleen, muscle, brain and blood, more abundantly from venous than from arterial, and probably existing in many cellular structures, whose composition is undetermined, although it is known to contain sulfur and phosphorus. It is soluble in ether, but insoluble in alcohol, which precipitates it from its ethereal solution. It reduces Fehling's solution, and glucose has been obtained from it in the form of its osazone. By heating with alkaline solutions and cooling it solidifies to a jelly.

The yellow coloring matter of the plasma and serum appears to belong to the class of luteïns, or lipochroms, which exist in fats, corpora lutea, egg-yolks, etc. A coloring-matter has been obtained from the serum of ox blood, which, in amylic alcohol solution, gives a spectrum of two bands, one covering F, the other between F and G.

Extractives.— The most abundant are urea, creatin, and salts of uric, carbamic, paralactic and hippuric acids; also, pathologically, xanthin bases, leucin, tyrosin and biliary salts and pigments. Urea is present in human blood in the proportion of 0.14 to 0.4 p/m; more abundant in the blood of the splenic, portal and hepatic veins than in that of the carotid artery; more abundant in placental blood, 0.28 to 0.62 p/m. In animals the proportion rapidly increases after nephrectomy, reaching 2.06 to 2.76 p/m in 27 hours. In human blood the amount is greatly increased in cholera, 2.4 to 3.6 p/m, and, particularly, in nephritis, 15.0 p/m.

Mineral Salts.—The serum contains a somewhat smaller quantity of mineral material than the plasma, a part of the calcium salts having passed into the clot. The total ash of the serum equals 8.3 to 9.2 p/m. In composition it does not vary greatly in different animals. In 1000 parts of human blood serum there are: $K_2O$–0.387 to 0.401, $Na_2O$–4.290, CaO–0.155, MgO–0.101, Cl–3.565 to 3.659, besides phosphoric acid, and traces of silicon, fluorin, iron, manganese, copper and ammoniacal compounds. The most abundant constituent of the ash is sodium chlorid, 60 to 70 per cent. of the ash. The calcium and magnesium are probably present as phosphates, and the former also as chlorid, the sodium and potassium as chlorids, phosphates and carbonates or bicarbonates. The amount of base present is in excess of the amount of acid, therefore a part of the bases must be present as carbonates or in organic combination. The presence of carbonates is demonstrated. The organic acids above mentioned are contained in the plasma in saline combination; and the existence of mineral elements in protein combination is shown by the fact that the mineral constituents are not completely removable by dialysis.

## BLOOD CORPUSCLES.

The corpuscular elements of the blood are of three kinds: the **red corpuscles**, the **white corpuscles**, or **leucocytes**, and the **plaques**, or **platelets**.

The **red corpuscles** are separated from the plasma by the methods given above. As they are heavier, they sink more rapidly than the other corpuscular elements, and are consequently found in the lower part of the deposit. Their variations in size, shape and number have been the subject of much careful study. Suffice it to say here that in man they are rounded bi-concave discs, non-neucleated, having an average diameter of 7 to 8 $\mu$ ($\mu$=micro-millimeter=0.001 mm.), and existing in the blood in the average number of 4 to 5 millions in 1 cubic millimeter. In other mammals, except camels, they have the same shape as in man, but differ in size, while in camels, birds, fishes and reptiles, they are oval and neucleated.

**Composition.**—Analyses of human blood corpuscles show them to contain 681.63 to 687.86 p/m of water, and 318.37 to 312.14 of solids. The corpuscles of animals contain a larger proportion of solids: pig—374.38 p/m, ox—408.14, horse—386.82, dog—372.85. In the solids the proportion of organic constituents to mineral salts is much greater in the corpuscles than in the plasma. The 318.37 and 312.14 p/m of solids in the above analyses contain respectively 311.1 and 303.17 of organic constituents and 7.36 and 8.97 of mineral. The solids consist of a proteid coloring matter, containing iron, **hæmoglobin**; albumens, including a nucleoalbumen and a globulin; lecithins, cholesterol, fatty acids, and salts.

On contact with water, by alternate freezing and thawing, by agitation with ether or with chloroform, or by the action of bile, the corpuscles swell and give up their coloring matter, which goes into solution, leaving the **stroma**, a colorless mass, which may be made to retract to the original size and shape of the corpuscle by the action of carbon dioxid, dilute acids, acid salts and other agents. This liberation of the pigment is referred to as "lakeing," or "lake coloring" (lakfarben), from the resemblance of the product to the pigments called lakes.

**Blood Coloring Substances.**—The red color of the blood depends upon the presence in the red corpuscles of a coloring matter, **hæmoglobin**, which exists in the two forms of **hæmoglobin** and **oxyhæmoglobin**. In what condition this pigment exists in the corpuscles is not clearly established. That it exists in some form of combination may be inferred from the facts that in the corpuscles it is insoluble in water, while free hæmoglobin, that of many animals at all events, is readily soluble; that hæmoglobin is crystalline, while

no crystalline structure can be made out in the corpuscles; that the oxy-compound in the corpuscles gives off its oxygen in a vacuum more readily than ordinary oxyhæmoglobin does; that the pigment in the corpuscles decomposes hydrogen peroxid without itself suffering oxidation, which is not the case with hæmoglobin; and that the native substance is more resistant to the action of reagents than free hæmoglobin. It certainly exists in the corpuscles in two forms of oxidation, one yielding hæmoglobin, and largely predominating in the blood in asphyxia, the other yielding oxyhæmoglobin, and largely predominating in arterial blood; the proportion of the two in venous blood being intermediate between the above. To the former of these combinations the name phlebin has been given, to the latter the name arterin.

**Hæmoglobin — Reduced Hæmoglobin** — exists in very small amount in arterial blood, and almost exclusively in the blood after death from asphyxia. It is more soluble and more difficultly crystallizable than oxyhæmoglobin, but isomorphous with it, although the crystals are darker in color. Its aqueous solution is purple, and gives a spectrum of a single broad band, covering D, and about three-fourths of the space between D and E. The violet end of the spectrum is less absorbed than with oxyhæmoglobin solutions of corresponding concentration (No. 1, Fig. 37, p. 547). It absorbs oxygen rapidly from air, with formation of oxyhæmoglobin. Hæmoglobin is obtained from oxyhæmoglobin by bringing its solution into a vacuum, by passing indifferent gases through it, or by the action of reducing agents, such as Stokes' reducing reagent, consisting of an ammoniacal solution of ferrous tartrate.

**Oxyhæmoglobin**—is the form in which the blood-coloring matter is usually obtained. The hæmoglobins from the blood of different animals differ from each other in several particulars; in crystalline form, in solubility, and in chemical composition. The most usual crystalline form, including that of human hæmoglobin, is in rhombic prisms or needles, but hæmoglobin from guinea pig's blood crystallizes in rhombic octahedra, and that from the squirrel in hexagonal plates. They differ also in the facility with which the crystals are formed, which is inversely as their solubilities. The hæmoglobin of the blood of the horse and guinea-pig are sparingly soluble and crystallize easily, those of human blood, ox blood and pig's blood are very soluble, and crystallize with difficulty. The crystals of oxyhæmoglobin are bright-red in color, and are doubly refracting. They contain from 3 to 10% of water of crystallization. In some hæmoglobins there are two atoms of sulfur to each atom of iron, in others there are three. The hæmoglobins of most animals contain carbon, hydrogen, nitrogen, iron, sulfur, and oxygen; but those of certain birds

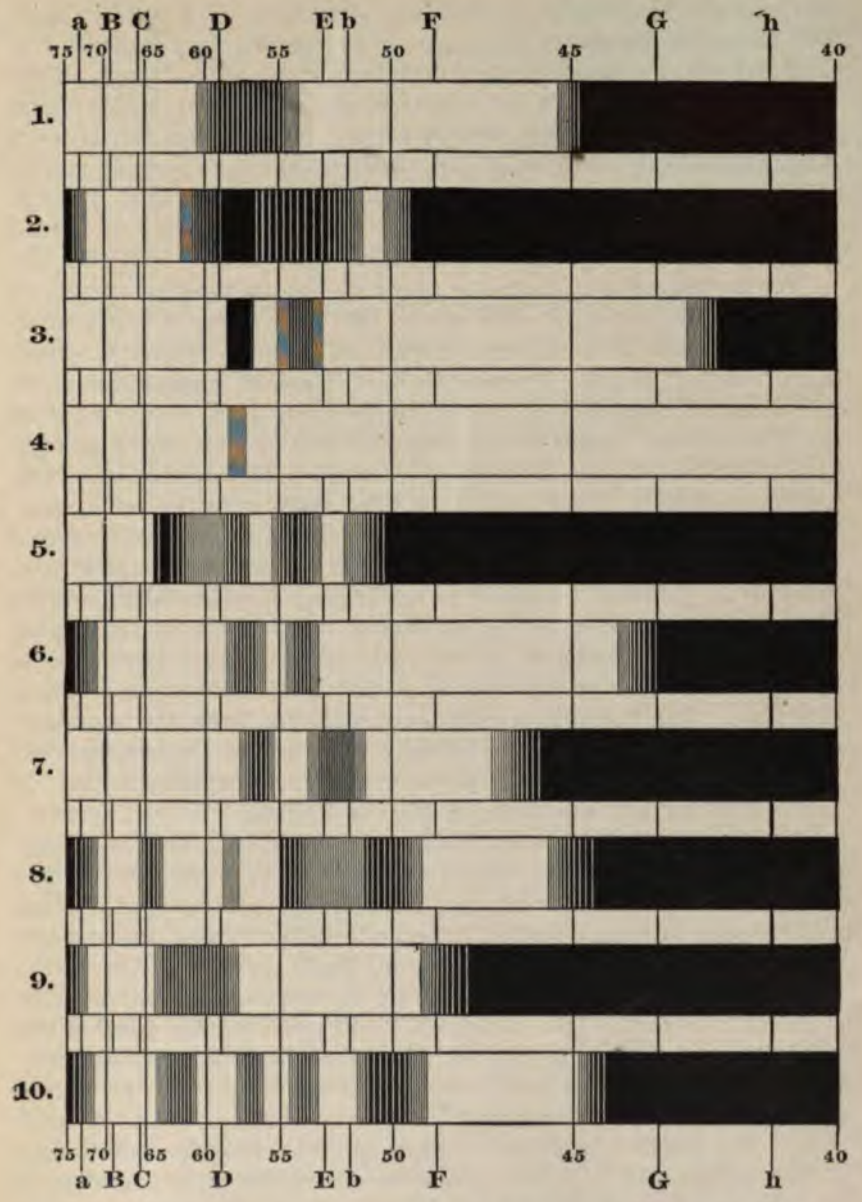



FIG. 37. Spectra of: (1) Reduced hæmoglobin; (2) Oxyhæmoglobin, concentrated; (3) Same, dilute; (4) Same, very dilute; (5) Methæmoglobin, in faintly alkaline solution; (6) Carbon monoxid hæmoglobin; (7) Hæmochromogen, in alkaline solution; (8) Hæmatin, in acid solution; (9) Hæmatin, in alkaline solution; (10) Hæmatoporphyrin, in acid solution.

also contain phosphorus, probably in the form of a nucleic acid. The molecular weight of hæmoglobin is certainly very large; a formula for that from dog's blood has been given as $C_{855}H_{1355}N_{231}FeS_3O_{241}$, corresponding to a molecular weight of 14,129; which must, however, be accepted with some reserve. Oxyhæmoglobin is more readily soluble in dilute acids and alkalies than in pure water, insoluble in alcohol, ether, chloroform, benzene, or carbon disulfid. When dried in vacuo at the ordinary temperature, it may be heated to 115° without suffering decomposition.

When hæmoglobin from the blood of the ox absorbs oxygen to form oxyhæmoglobin, it does so in the proportion of 1.34 cc. of oxygen for each gram of hæmoglobin (at 0° and 760 mm.), which, calculated for weight, is equal to five atoms of oxygen for three molecules of hæmoglobin. The combination is a "loose" one, in that the combined gas is readily given off in a vacuum, or by passage of an indifferent gas through the solution. Hæmoglobins, when heated in solution to 60° to 70°, or when acted upon by acids, alkalies, or certain metallic salts, are decomposed into a protein and a colored derivative containing iron. The protein, called globin, is probably a globulin, insoluble in water, but very soluble in dilute acids or alkalies, insoluble in ammonia in presence of ammonium chlorid. It is coagulated by heat, but the coagulum is soluble in acids. Nitric acid precipitates it in the cold, but not from warm solutions. The ferruginous pigment resulting from the decomposition differs according to the degree of oxidation of the hæmoglobin. If oxygen be excluded, the product is hæmochromogen, but in presence of oxygen hæmatin (p. 550) is formed.

The spectrum of oxyhæmoglobin varies with the degree of concentration of the solution. When a solution, sufficiently concentrated to be opaque when observed spectroscopically in a layer of a given thickness, is gradually diluted it first allows portions of the red and orange to pass. On further dilution, light appears in the green, leaving a single broad band extending from about midway between C and D to beyond b (No. 2, Fig. 37). On still further dilution this band divides into two, giving the characteristic oxyhæmoglobin spectrum, consisting of two bands, one ($\alpha$) between D and E, and resting on D, the other ($\beta$) extending from about midway between D and b to b. The band $\alpha$ is narrower, darker and more sharply defined than $\beta$ (No. 3, Fig. 37). This spectrum is still visible with a solution of 0.1 p/m in a layer 1 cm. thick. With further dilution the band $\beta$ disappears first (No. 4, Fig. 37). On addition of reducing agents the spectrum changes to that of hæmoglobin (No. 1, Fig. 37).

**Pseudohæmoglobin.** — When a solution of oxyhæmoglobin is reduced by ammonium sulfid until it gives the spectrum of hæmo-

globin, it will still give off oxygen in the vacuum. In this condition it is, therefore, not completely reduced, and the intermediate form of oxidation which is supposed to exist in the solution has been called pseudohæmoglobin.

**Methæmoglobin**—is a product of oxidation of hæmoglobin, containing the same proportion of oxygen as oxyhæmoglobin, but in state of firmer chemical union, which may be expressed by writing the formula of oxyhæmoglobin as $Hb\begin{smallmatrix}O\\|\\O\end{smallmatrix}$, and that of methæmoglobin as $Hb\begin{smallmatrix}O\\O\end{smallmatrix}$. Methæmoglobin occurs in transudates and exudates, and in the urine in hæmaturia and hæmoglobinuria, and, particularly, in poisoning by poisons such as potassium chlorate, amyl nitrite and the alkaline nitrites. It is formed from hæmoglobins when blood is kept in hermetically sealed vessels, or by the action upon them of many oxidizing agents, ozone, permanganates, chlorates, nitrites, etc. It crystallizes in red-brown, hexagonal prisms, needles or plates, which form a brown-red solution with water, which changes to bright-red with alkalies. It is very soluble in water. Its neutral, or faintly alkaline or acid, solutions give a spectrum of a single band between C and D, nearer to C and united by a space of partial absorption with the $\alpha$ band of the oxyhæmoglobin spectrum, which is also present (No. 5, Fig. 37). By the action of reducing agents upon faintly alkaline solutions the spectrum changes to that of reduced hæmoglobin.

**Carbon Monoxid Hæmoglobin**—is a form of combination of hæmoglobin existing in the blood of those poisoned by carbon monoxid, or by illuminating gas, and whose production is the cause of death by that poison. It is a definite compound, containing one molecule of CO for each molecule of hæmoglobin, and, being more stable than oxyhæmoglobin, is not oxidized in the lungs, and thus destroys the oxygen-carrying function of the blood coloring-matter. It is formed by passing CO through blood, or through a solution of hæmoglobin or of oxyhæmoglobin. It crystallizes readily in forms isomorphous with oxyhæmoglobin, but more bluish in color, more stable, and less soluble. Its solutions are bright-red in color and give a spectrum of two bands, resembling that of oxyhæmoglobin, but differing therefrom in that the two bands are of equal intensity, are somewhat differently placed (No. 6, Fig. 37), and also in that reducing agents do not change the spectrum to that of reduced hæmoglobin. Carbon monoxid blood, when mixed with an equal volume of NaHO solution (sp. gr. 1.3) forms a bright-red mass, while normal blood, similarly treated, forms a dirty-brown mass with a greenish tinge.

**Carbon Dioxid Hæmoglobin.**—A solution of hæmoglobin shaken with a mixture of oxygen and carbon dioxid takes up both gases, forming molecular combinations with each. It is supposed that the carbon dioxid combines with the protein factor of the coloring matter. Carbon dioxid alone is also absorbed by hæmoglobin solutions, and the spectrum is then that of reduced hæmoglobin, while a part of the coloring matter is decomposed with separation of globin.

**Hæmochromogen**—is formed by the action of NaHO upon hæmoglobin in complete absence of oxygen, or by the action of reducing agents upon hæmatin in alkaline solution. It gives a spectrum of two bands, resembling the oxyhæmoglobin bands in relative intensity, but placed nearer to the violet end of the spectrum (No. 7, Fig. 37).

**Hæmatin**—is produced by decomposition of oxyhæmoglobin by alkalies. It exists in old transudates, is formed by the action of the gastric and pancreatic secretions upon hæmoglobin, and is met with in the urine in poisoning by hydrogen arsenid. It is amorphous, blue-black, insoluble in water, dilute acids, alcohol, ether, or chloroform, sparingly soluble in hot glacial acetic acid, soluble in acidulated alcohol or ether, very soluble in dilute alkalies. Its alkaline solutions are dichroic, red by reflected light, green by transmitted; its acid solutions are brown. The formula usually ascribed to it is $C_{32}H_{32}N_4FeO_4$. In acid solution in alcohol or ether it gives a spectrum of four bands (No. 8, Fig. 37): $\alpha$, the darkest, near to C, and extending about one-third to D; $\beta$ resting on D, narrower and paler than $\alpha$; $\gamma$ between D and E, nearer to E, broader and paler than $\alpha$; $\delta$ the broadest of the four, a pale band whose center is midway between b and F, and covering about three-quarters of the space. The interval between $\gamma$ and $\delta$ is partly absorbed. In alkaline solution hæmatin gives a spectrum of a single band, extending from near C to beyond D (No. 9, Fig. 37).

**Hæmin**—is a compound of hæmatin with chlorin or iodin, whose formation is utilized as the most characteristic test for blood. It forms red-brown crystals, which, when perfect, are rhombic prisms, insoluble in water, alcohol, ether, dilute acids or chloroform, soluble without decomposition in hot glacial acetic acid, soluble with decomposition in acidulated alcohol or in dilute NaHO solution. The crystals, known also as **Teichmann's crystals**, are best obtained as follows: a fragment of the dried stain is placed upon a glass slide, upon which a very minute drop of dilute sodium chlorid, or iodid, solution has been previously evaporated, and covered with a cover-glass. Glacial acetic acid is then run in beneath the cover, and the slide cautiously heated over a very small flame until bubbles just begin to appear, when the slide is raised about three inches above

the flame and kept warm for a few minutes, while the loss of acid by evaporation is supplied by fresh glacial acetic acid placed at the edge of the cover with a slender glass rod. The slide is now allowed to cool, and, during cooling and evaporation of the acid, examined with a one-fifth inch objective. The crystals are usually found near the edge of the cover, or imprisoned in the remains of the clot, and are generally all in a small space, while the remainder of the preparation is free from them. The acid must not be allowed to boil, or the crystals may be mechanically carried out from under the cover. The formation of the crystals under these conditions may be accepted as certain evidence of the presence of blood-pigment, but their non-formation is not evidence of its absence. They cannot be obtained if the stain contains iron-rust, or has been treated with chlorin or with certain kinds of soap.

**Hæmatoporphyrin**—is an isomere of bilirubin (pp. 528, 531), therefore containing no iron, $C_{16}H_{18}N_2O_3$, and is derived from hæmatin: $C_{32}H_{32}N_4FeO_4+2H_2O=2C_{16}H_{18}N_2O_3+Fe$. It occurs normally in urine in minute quantity, and is notably increased in poisoning by sulfonal. It forms a compound with HCl which crystallizes in long, red-brown needles, and is precipitated from its HCl solution by partial neutralization and addition of sodium acetate, as an amorphous, brown powder. It is soluble in dilute acids or alkalies, the acid solutions having a purple color, and the alkaline solutions being red. Reducing agents convert it into urobilin, and when injected into the circulation of rabbits it is partly eliminated in that form. In acid solution it gives a spectrum of two bands (No. 10, Fig. 37), $\beta$, the narrower and less intense, between C and D, nearer to D; and $\alpha$, much darker and broader, about midway between D and E, with a space of less complete absorption extending nearly to D. In alkaline solution it gives a four-band spectrum, one ($\alpha$) between C and D, a broader one ($\beta$) over D, a third ($\gamma$) between D and E, extending nearly to E, and a fourth ($\delta$) between b and F. On addition of alkaline zinc chlorid solution the bands $\alpha$ and $\delta$ gradually fade out, leaving $\beta$ and $\gamma$.

**Hæmatoïdin**—another decomposition-product of hæmoglobin, is identical with bilirubin (p. 528).

The **stroma** (p. 545) of the red corpuscles contain the constituents other than the coloring matter, and probably a portion of the salts. The principal organic constituents are: a globulin, which has been called cell-globulin, and a nucleoalbumen. The non-nucleated corpuscles of the mammalia contain no nucleoproteid, although the nucleated corpuscles of the birds and fishes contain a nuclein and a nucleoproteid, which forms a mucilaginous solution with a 10 per cent. NaCl solution. The proportion of albumens to hæmoglobin is

much greater in nucleated than in non-nucleated corpuscles. Thus human corpuscles contain in 1000 parts 868 to 943 of hæmoglobin against 122 to 51 parts of albumens, while in serpents' blood the proportion is 467 hæmoglobin to 525 of albumens. The red corpuscles of frogs' blood also appear to contain fibrinogen, or a related protein. Lecithins exist in human corpuscles, in the proportion of 3.5 to 7.2 p/m, and cholesterol to the amount of about 2.5 p/m. The total ash of human corpuscles, including the iron derived from the hæmoglobin and the phosphoric acid derived from the lecithins, constitute 3.5 to 3.7 p/m of their weight. The salts vary in different animals. In the corpuscles of the pig, ox, horse and dog the sodium compounds are notably more abundant than those of potassium, while human corpuscles contain sodium compounds equivalent to 0.24 to 0.65 $Na_2O$, and potassium compounds equivalent to 1.41 to 1.59 $K_2O$. The mineral salts present are potassium and sodium chlorids and phosphates, with mere traces of magnesium salts. Calcium compounds, so important in the serum, are entirely absent from the corpuscles.

The **leucocytes, or white corpuscles,** are rounded, colorless protoplasmic masses, endowed with the power of amœboid movement, having no limiting membrane, which, on addition of water or of 1% acetic acid, are seen to have from one to four nuclei, round or irregular in outline. They are less numerous than the red corpuscles, the average proportion between the two being from 1:350 to 1:500; but their number varies greatly under varying normal, as well as pathological, conditions. Histologically they are divided into several groups, the members of which differ from each other in size, in appearance, and in their behavior towards staining agents. Although no differences in chemical composition between these several kinds of white corpuscles are known to exist, the differences in their behavior towards stains, which are in reality chemical reagents, render it highly probable that they are not chemically identical. Indeed our knowledge of the chemical composition of the leucocytes is fragmentary. The constituents of the protoplasm differ from those of the nuclei. The bulk of the protoplasm consists of proteins, among which are a substance, probably a nucleoproteid, **nucleohiston**, soluble in water and precipitated by acetic acid; another nucleoproteid which swells to a mucilaginous mass on contact with alkalies or salt solution, and is very similar to, if not identical with, the **hyaline substance of Rovida,** which exists in pus cells; and a globulin, supposed to be serum-globulin. Among these proteins is the zymogen of thrombin, which probably is one of the nucleoproteids. Glycogen and fat are also present in small amount. A phosphorized and nitrogenized body has also been obtained from the

leucocytes, and probably exists in their protoplasm, which is one of the **protagons**, important constituents of nerve and brain tissues, which, on boiling with baryta water, are decomposed into **cerebrins**, nitrogenized but non-phosphorized bodies, and the constituents of the lecithins: fatty acids, glycerophosphoric acid and cholin.

The **nuclei** of the leucocytes are rich in nucleoproteids, and also contain nucleins and nucleic acids.

But little is known of the chemical composition of the **plaques** beyond the probability that they consist largely of a combination of albumen and nuclein.

## THE BLOOD AS A WHOLE.

The color of the blood is bright-red if arterial, bluish-red if venous, bright cherry-red in poisoning by carbon monoxid, brownish-red in poisoning by potassium chlorate, anilin, or nitro-benzene, dark purple-red after death from asphyxia. It is opaque, even in thin layers. It is salty in taste; and its odor is similar to that of the animal, being more pronounced after addition of $H_2SO_4$; sp. gr. 1.045 to 1,075; reaction alkaline. The alkalinity of the blood depends in part upon the presence of alkaline bicarbonates (p. 565) and phosphates, and in part upon alkaline protein compounds. The normal degree of alkalinity of human blood has been given by different observers as equal to from 3.38 to 5.95 p/m of sodium carbonate, or 2.55 to 4.5 p/m of sodium hydroxid. Usually the limits of normal variation are placed at 3.3 to 5.3 p/m $Na_2CO_3$, or 2.5 to 4.0 p/m NaHO. The alkalinity of the blood rapidly diminishes after its removal from the circulation, by reason of the generation of acids, which has led to results lower than the above, some authors giving the normal limits as low as 1.8 to 3.0 p/m NaHO. Normally the degree of alkalinity is greater in men than in women and children; and is diminished after violent muscular activity. It increases with activity of the stomach digestion, and subsequently diminishes from absorption of hydrochloric acid and peptones from the intestine. Pathologically, it is diminished in anæmia, leukæmia, uræmia, diabetes, hepatic diseases, high fevers, and in acidism due to administration of mineral acids or to the generation of organic acids in the body. It is increased by administration of alkalies, by cold baths, and in phthisis, erysipelas, and septicæmia (p. 555).

The change of **coagulation**, which the blood undergoes shortly after being drawn from the blood-vessels, is a chemical phenomenon dependent upon physical conditions, the precise nature of which has not been satisfactorily explained. Coagulation takes place with dif-

ferent degrees of rapidity in the blood of different animals, and with different individuals of the same race. In human blood it usually begins in 2–3 minutes after the blood is drawn, and it results in the formation of a jelly-like mass in 7–8 minutes. If it take place rapidly the clot is uniform in appearance, but if it be delayed the corpuscles sink, the red more rapidly than the white, and the upper part of the clot, the "buffy coat" or "crusta phlogistica," is pale in color, and contains few red corpuscles and many white ones. Coagulation is delayed by cold, diminished oxygen-content, increased carbon dioxid, the presence of acids, alkalies, ammoniacal salts, oxalates, fluorids, egg-albumin, sugar, dextrin, glycerol, albumoses, snake-poison, toxalbumins, or an infusion of the mouth of the leech, or by collection in oil. It is accelerated by warmth, contact with air, whipping, contact with solids to which it adheres, or addition of leucocytes, nucleoproteids, or extracts of lymphatic glands, testicles, or thymus.

As to the cause of coagulation, and particularly, its non-coagulation in the vessels during life, opinions differ. The following facts, in addition to others already discussed, bear upon the question: (1) the blood does not coagulate while in contact with living, healthy blood-vessels; (2) it remains fluid in a ligated section of a vein, removed from the body; (3) it coagulates rapidly when collected in a vacuum over mercury; (4) it does not coagulate when collected through an oiled or vaselined canula into a similarly prepared vessel; (5) in such vessels it does not coagulate when stirred with an oiled or vaselined glass rod; but, (6) it does coagulate when stirred with an unoiled rod; (7) under the conditions of 5 and 6, coagulation begins when a film of solid forms upon the surface by drying, or if a small quantity of dust be present in the oil or vaseline; (8) it coagulates in living blood-vessels when their internal surfaces become roughened, or in presence of foreign material with rough surfaces. From these facts it may be inferred that the change does not depend upon the presence of air, but that it does depend in some way upon the physical condition of adhesion. It is generally admitted, also, that the corpuscles, particularly the leucocytes and plaques, contain a zymogen, prothrombin, from which an enzym, thrombin, is derived in the presence of calcium salts, and that thrombin in some unknown way, possibly by hydrolytic splitting, produces fibrin from fibrinogen. It is known that during coagulation notable destruction of leucocytes and of plaques occurs, and it is believed that this breaking down is attended by a chemical action between the nucleoproteid, prothrombin (nucleohiston ?), and the calcium compounds, with formation of thrombin; and that coagulation does not occur in the healthy vessels, because this disintegration of corpuscular elements

only takes place to a limited extent, and the small amount of thrombin so produced is destroyed, probably by an action of the liver.

## CHEMICAL EXAMINATION OF BLOOD.

The more accurate methods of blood analysis, including those for the examination of the blood-gases, which are used in scientific investigation, are quite intricate, and demand close observance of details and considerable manipulative skill. As their description would require much space, and as they are not used for clinical purposes, the student is referred to more comprehensive treatises for an account of them. While the methods of microscopical examination of the blood for clinical purposes have been greatly perfected, and have led to valuable results, there is practically nothing worthy of consideration in the way of chemical methods for this use. We have accurate methods for determining the physical quality of specific gravity, methods of determining the reaction, which leave much to be desired, and methods of determining the quantity of hæmoglobin, some of which are accurate but difficult, others more easily conducted, but affected with large factors of possible error.

**Specific Gravity.**—(1) *Hammerschlag's method*, which depends upon the fact that a drop of an immiscible liquid will remain suspended in a liquid whose sp. gr. is equal to its own. A mixture is made of chloroform, sp. gr. =1.526 and benzene, sp. gr. =0.889, in such proportions that the sp. gr. of the mixture is about 1.050 to 1.055, and a drop of the blood is allowed to fall into it. If the blood-drop sink more benzene is added, if it float, more chloroform, until the blood-drop remains suspended. The sp. gr. of the mixture is then determined, and is equal to the sp. gr. of the blood.

(2) *By direct weighing.*—Capillary tubes are used, drawn out at the ends, which are about 12 cm. long, and have internal diameters of 1.5 mm. in the middle, and 0.75 mm. at the ends. These are weighed empty, and also filled with water; the difference being the weight of water which the tube contains. The water is then blown out, and the tube filled with blood and again weighed. Subtraction of the weight of the empty tube from this last weight gives the weight of the blood. The sp. gr. is calculated, as usual, by dividing the weight of the blood by that of the water.

**Reaction.**—Determinations of the degree of alkalinity of the blood must be made as soon as possible after the sample is removed from the circulation to avoid as much as possible the minus error due to diminution of alkalinity (p. 553). *Lowy's method* is probably the least open to objection. A flask is used having a long neck, upon

which are two marks, one at 45 cc., the other at 50 cc. This is filled to the 45 cc. mark with a one-fourth per cent. solution of ammonium oxalate, and 5 cc. of blood are drawn directly from the blood-vessel into it to the 50 cc. mark, and the contents mixed. The liquid is then titrated with a N/25 solution of tartaric acid (3 gm. tartaric acid to the litre), using a lacmoid paper saturated with strong magnesium sulfate solution as an indicator. One cc. of this solution is equivalent to 0.0016 gm. of NaHO; therefore the number of cc. used, multiplied by 200, gives the alkalinity in parts p/m of NaHO.

**Hæmoglobin.**—Of the chemical methods of determination of the quantity of hæmoglobin the best consists in incinerating the dried blood and determining the quantity of iron, from which the proportion of hæmoglobin is calculated.

Of the optical methods the most accurate is probably the spectrophotometric method of Vierordt, or one of its modifications, which depends upon measurement of the proportion of light of a certain wave-length absorbed in passing through a layer of a definite thickness of the blood, diluted in known proportion. This method, besides yielding accurate results, has the advantage that by it the proportions of oxyhæmoglobin, reduced hæmoglobin and carbon monoxid hæmoglobin may be determined in the same sample. It requires, however, a spectroscope specially adapted to the purpose. **(See Neubauer and Vogel, Harnanalyse, 10th ed. pp. 680–696.)**

**Colorometric methods depend upon comparison of depth of color of the specimen of unknown content with standards of known content or value. When such comparisons are made between layers of equal thickness of solutions equal in transparency of the same substance, very slight differences in shade may be easily distinguished, and accurate results may be obtained. These conditions are fulfilled in the hæmatinometer of Hoppe-Seyler and its modifications, in which the depth of color of the blood, diluted in known proportion, is imitated in the comparison apparatus, with a solution of pure, crystallized hæmoglobin of known strength. When the two samples have precisely the same shade, the proportion of hæmoglobin in the comparison sample of known content will equal that in the diluted blood. To avoid the inconvenience of preparing the hæmoglobin solution, which does not keep, a solution of carbon monoxid hæmoglobin of known content, which is permanent, may be used, if the precaution be taken of converting the hæmoglobin in the blood sample into carbon monoxid hæmoglobin by passing CO through it before making the comparison.**

**The different forms of clinical colorimeters, known as hæmoglobinometers, such as Fleishl's, Oliver's, Taylor's and Gower's, are**

all open to the objection that the comparison of tint is made with colored glasses, or with solutions of colored substances other than the blood-coloring matter, and consequently not identical in quality with it. While these instruments, and to a less degree, the forms of clinical blood-testers depending upon determinations of opacity or of specific gravity, may afford comparative results of value to the clinician, they are not to be depended upon for accurate work. For the technique of clinical blood examination the student is referred to the excellent article by Dr. Camac in Wood's Handb. of the Med. Sc. 2d Ed. II. 37–71.

## CHANGES IN COMPOSITION OF THE BLOOD IN DIFFERENT PARTS OF THE CIRCULATION.

As the blood-circulation is the channel through which the materials for the nutrition and functioning of the different parts of the body are carried to them, and by which the waste products of their activity are removed, a study of the variations in the composition of the circulating medium in its passage through different organs under varying conditions may well be expected to throw light upon the nature of normal and pathological chemical processes. Unfortunately, the difficulties in the way of experimentation are great, and but little has yet been accomplished; the chief impediment being the difficulty of obtaining specimens of blood from the two sides of the organ under investigation, which are comparable with each other. The abstraction of any notable quantity of blood from the circulation at a given point, or the ligation of an efferent vessel and the consequent stasis in the organ at once produce pathological conditions.

The situations which have been the most frequently under investigation in this regard are the hepatic, the pulmonary and the renal circulations. Changes in the blood in the last named may be inferred from changes in the composition of the urine, and will be considered under that head. The chemistry of the blood changes in the lungs is a portion of that of respiration (see pp. 560, 566).

**Changes in the Liver.**—As all the products of digestion which are absorbed from the alimentary canal by the blood are carried by the portal vein to the liver, mixed with the venous blood from the spleen and pancreas, and, after passage through the hepatic circulation, are discharged into the general circulation by the hepatic veins, and as, moreover, the liver is furnished with blood for its own nutrition by a separate supply through the hepatic artery, it would seem, a priori, that the liver should act as an adjunct to the digestive apparatus in being the seat of further chemical changes in the

products of digestion, preparatory to their utilization in the tissues. That substances absorbed from the intestine are modified chemically in their passage through the liver is shown by the fact that many poisons, not only metallic poisons, such as arsenic, copper, and lead, but also alkaloidal poisons, such as morphin, strychnin, atropin, etc., when injected into the portal vein, act with only one-half to one-third the intensity as when injected in like amount into the jugular vein. The putrid products of intestinal origin are also modified in the liver. The normal portal blood of the dog has double the toxic power of the blood of the hepatic veins of the same animal when injected into the peripheral circulation of rabbits. That synthetic chemical actions take place in the liver is undoubted. The phenols produced in intestinal putrefaction there combine to form the more complex ester-sulfuric acids, certain ammoniacal compounds are converted into urea, and, probably, into uric acid. Little or nothing is, however, known of the nature of the processes to which the proteins and fats are subjected in the liver; or of the products of such actions, if any such occur. The action of the liver upon the carbohydrates has been better studied, and the glycogenic function of that organ is well established.

Glycogen is a substance closely related chemically to starch (p. 275) which exists in many situations in the body, notably in the liver, in muscular tissue, and in embryonic tissues, in each of which it is formed. The quantity of glycogen in the liver tissue is influenced by several conditions. The nature of the diet has an influence upon the quantity of glycogen, not only in the liver, but also in the muscles. The usual proportion in the liver is 12 to 40 p/m. With a diet rich in carbohydrates it may rise to 120 to 160 p/m. In starvation it disappears from the liver first, and subsequently from the muscles; and that more rapidly in animals of small size than in large ones. When food is taken the glycogen-content increases, to reach its maximum about 14 to 16 hours after the meal. The proportion of glycogen in the liver is inversely proportionate to the amount of muscular activity, and with violent exertion it disappears entirely. This result is reached in rabbits under the influence of strychnin, administered to the extent of causing tetanic convulsions, in from 3 to 5 hours. In fevers, also, the glycogen-content of the liver is diminished.

Bearing upon the origin of liver-glycogen, it has been found to be increased in amount after administration of monosaccharids and disaccharids, particularly the former, dextrins, starches, glycerol, gelatin, arbutin, erythrite, quercite, dulcite, mannite, inosite, glycols, saccharin, glycocoll, ammonium salts, amids, narcotics, hypnotics, and antipyretics. The principal glycogen-formers are undoubtedly

the carbohydrates, although it is also formed from proteins. The form in which the carbohydrate material is utilized by the liver is that of the three monosaccharids, glucose, fructose, and galactose, which are the products of intestinal digestion. Of the three disaccharids, cane sugar and milk sugar are eliminated unchanged if injected into the circulation, and consequently require the inversion to which they are subjected in the intestine before they can be utilized. Maltose, on the other hand, is inverted in the blood, and is probably absorbed from the intestine in its own form. The conversion of the hexoses into glycogen is a simple process chemically: $n C_6H_{12}O_6 - n H_2O = n C_6H_{10}O_5$, but by what mechanism it is brought about in the liver cells is not known. That glycogen also originates from some proteins is demonstrated by the fact that, not only is glycogen produced, but the urine also contains sugar in diabetics from whose diet carbohydrates have been completely excluded; although glycogen may also be produced from the fats in the animal economy, as it certainly is in the vegetable. Probably a part, at least, of this glycogen has its origin in the decomposition of glycoproteids, but possibly, by some unknown processes of decomposition and synthesis, other proteins may be decomposed into a carbohydrate and a nitrogenized factor. The glycogen existing in the muscles is probably not carried to them by the blood but formed in them. This is certainly the case in the embryonic tissues, which are very rich in glycogen.

That glycogen is converted into glucose in the liver after death is certain, and that a similar change occurs during life, probably under the influence of a diastatic enzym, is believed by most observers, though doubted by some. When the liver is more or less completely excluded from the circulation, in geese, the sugar rapidly disappears from the blood, or is at least diminished by one-half or one-third.

The part played by the liver, if any, in the different forms of glycosuria (p. 607) is still an open question, although it is certain that it is not the same in all the conditions in which that symptom exists. The blood normally contains 1.5 p/m of glucose, which is also present in traces in normal urine (pp. 543, 596), but when the proportion in the blood reaches 3 p/m the urine contains notable quantities of sugar; glycosuria exists. The power of the kidneys to prevent the passage into the urine of more than traces of sugar is therefore limited; and glycosuria may be caused either by a diminution of this power below the normal, or by an increase of sugar in the blood. The former condition is known to exist only in a form of artificial diabetes, produced by the administration of phloridzin, which is a glucosid yielding a hexose other than glucose (p. 413) on its decomposition, and causing the formation in the system of glucose from protein material. Other glycosurias depend upon hypergly-

kæmia. This may, in turn, be due to one of three causes, either (1) the passage from the alimentary canal, through the liver, and into the general circulation of an abnormally large amount of sugar; (2) the formation in the liver, or elsewhere in the system, of an increased quantity of sugar; and, (3) an inability on the part of the system to utilize the amount of sugar normally produced. The first cause is certainly operative in *alimentary glycosuria*, due to a diet inordinately rich in assimilable carbohydrates. It is probable that, even under normal conditions, a portion of the sugars of the portal blood pass through the liver unchanged, and with an increased richness of the portal blood in carbohydrates a larger proportion will naturally escape the retaining action of the perfectly normal liver. Or this power may be pathologically diminished, as is probably the case in the milder forms of diabetes, in which the glycosuria readily disappears upon regulation of the diet, and also in some forms of chronic poisoning. The second cause is operative in glycosuria attending cerebral and nervous lesions, including the artificial diabetes caused by puncture of the floor of the fourth ventricle. It is not possible to exclude this cause also, as one of the factors in the severer forms of true diabetes, in which the daily elimination of sugar may go as high as 500 to 1,000 grams. There is also diminution in the power of the system to consume the carbohydrates in true diabetes, as well as in the glycosuria attending diseases of the pancreas, and in the severe artificial diabetes following extirpation of that organ. It has even been suggested that the pancreas produces a glycolytic enzym, by which glucose is normally decomposed.

## CHEMISTRY OF RESPIRATION.

The function of respiration is a physico-chemical one, the purpose of which is the introduction of oxygen into the system, and the removal of carbon dioxid and water therefrom. In so far as it is chemical, the subject may be considered under the following heads: (1) changes in composition of the air; (2) changes in composition of the blood-gases in the lungs; (3) tissue-respiration.

**Changes in Air.**—The average composition of dry atmospheric air, in volumes, corrected for 0° and 760 mm. barometric pressure, is: Oxygen—20.95, nitrogen—79.02, carbon dioxid—0.03, disregarding traces of other gases. The proportion of carbon dioxid varies from the above percentage in confined spaces (p. 306), and the air always contains varying quantities of vapor of water (p. 103). The expired air varies somewhat in the relative proportions of its constituents. Its average composition is, however: oxygen—16.03,

nitrogen—79.59, carbon dioxid—4.38; and it is saturated with vapor of water at the temperature of the body, about 36°, and the barometric pressure. It will be seen that the proportion of nitrogen, which is a mere diluent, remains practically unchanged, and that the changes which the air undergoes in respiration consist of the subtraction of 4.92 volume-per cent. of oxygen, and the addition of 4.35 volume-per cent. of carbon dioxid and of a quantity of vapor of water, varying with the degree of saturation of the inspired air. With an increased degree of humidity of the inspired air the elimination of water by the skin and kidneys is increased.

That the oxygen taken into the system is utilized in processes of oxidation which take place in the tissues, and only to a limited extent in the lungs and blood, is now generally admitted. If the oxygen taken in were entirely used for the oxidation of carbon, and if there were no source of oxygen other than the inspired air, the volume of oxygen removed from the inspired air should equal the volume of carbon dioxid added to it, as one molecule of oxygen produces one molecule of carbon dioxid. But the volumes are not equal, and neither of the above conditions exists. All tissues and organic food constituents contain hydrogen as well as carbon, and a portion of the oxygen is used to oxidize this to water. On the other hand, they all contain oxygen, as well as carbon and hydrogen, which supplements the oxygen derived from the air. Thus 180 grams of glucose produces by complete oxidation 264 grams of carbon dioxid, and 108 grams of water, for which 288 grams of oxygen are required, of which the glucose itself furnishes 96 grams, or one-third of the amount:

$$\underset{180}{C_6H_{12}O_6} + \underset{192}{6O_2} = \underset{264}{6CO_2} + \underset{108}{6H_2O}$$

Moreover, carbon dioxid and water are not the only products of oxidation formed in the body: urea, for example, is a product of oxidation of the proteins. Thus the relation of oxygen consumed to carbon dioxid produced depends upon many conditions, and there is always an apparent loss of oxygen. This relation is known as the **respiratory quotient**, and is obtained by dividing the $CO_2$ produced by the $O_2$ consumed. Thus in the above proportions: $\frac{4.35}{4.9} = 0.88$. The fats contain 10.73 to 11.91% of oxygen, the proteins 21.5 to 23.5%, and the carbohydrates 51.17 to 53.33%, while the amount of oxygen required for the oxidation of their hydrogen is, for 100 parts each: of fats, 97.3 to 98.8; of proteins, 52.0 to 58.4, and of carbohydrates, 51.17 to 53.3. It is clear, therefore, that the carbohydrates contain sufficient oxygen for the oxidation of their hydrogen, while the proteins and fats require additional oxygen

for that purpose, and that, consequently, the respiratory quotient will vary with the composition of the diet. It also varies with the amount of muscular activity, increase of which is attended with increase of protein oxidation, and with marked increase of production of carbon dioxid.

In considering the method of interchange between the gases of the blood and those of the air, it must be remembered that this exchange takes place between the blood and the air contained in the alveoli, and that this is not completely changed in respiration. Therefore, the composition of the alveolar air, which is the mixture formed by diffusion between the air remaining in the alveoli after expiration with that taken in during inspiration, is of importance in connection with the method of gas interchange. The composition of alveolar air in the human subject can only be implied by calculation; but experiments upon animals have shown it to contain 3.6 to 3.8 volume-per cent. of carbon dioxid and about 16 volume-per cent. of oxygen, corrected for 0° and 760 mm.

**Gases of the Blood.**—The gases which the blood gives off when it is brought into a vacuum consist of oxygen, carbon dioxid, nitrogen, and traces of argon. The amount of nitrogen, including argon, is about the same in arterial and venous blood in different parts of the circulation, i. e., from 1 to 2 volumes in 100 volumes of blood. It probably takes no part in the chemical processes of the body. The blood-gases in which interest centers are, therefore, oxygen and carbon dioxid. The methods of absorption or elimination of these gases, and the form in which they exist in the blood may be either physical or chemical. That is to say, they may pass between blood and air by simple diffusion, or by a so-called "vitalistic" process, which, if it be not physical, must be chemical; and they may exist in the blood in simple physical solution, or in a form of chemical combination. To determine which of these methods are operative, and in what degree, is a subject requiring both physical and chemical investigation. We briefly recall here the laws governing the absorption of gases by liquids:

When a gas is in contact with a liquid it may either dissolve in or combine chemically with the liquid. In either case it is said to be **absorbed.** If in physical solution it is said to be **dissolved,** if in chemical combination it is said to be **combined.**

The **co-efficient of absorption** of a gas is the volume of that gas, reduced to 0° and 760 mm. Hg, absorbed by unity volume of the liquid under a pressure of 760 mm.; and it varies with the temperature. Thus the coefficient of absorption of carbon dioxid in water is 1.185 at 10°, which means that 1 cc. of water at that temperature, will absorb 1.185 cc. of carbon dioxid.

The *weight* of gas which a given *volume* of liquid will *dissolve* at a given temperature is directly proportionate to the pressure. But as the volume of a gas, at a given temperature, varies inversely as the pressure, the *volume* of gas dissolved is independent of the pressure; and the *density* of the dissolved gas is in constant relation to that of the undissolved gas in contact with it. Or, in other words, the *pressure* or *tension* of the dissolved gas is the same as that of the free gas in contact with it. If this equality be disturbed from any cause, as by variation of temperature, the gas passes into or out of solution, from the higher to the lower pressure.

The quantity of gas dissolved diminishes with increase of temperature, as the elastic force of the gas increases.

When several gases are dissolved in the same liquid, each is dissolved as if it were alone, its volume being estimated at the pressure which belongs to that gas in the mixture. This *partial pressure* is to the total pressure as the volume of the gas in question is to that of the mixture under the same conditions. The partial pressure may be calculated by the formula $PP=\frac{V\times P}{100}$, in which V is the volume-per cent. of the gas in question in the mixture, and P the total pressure in mm.

The pressure (tension) of a gas in solution may be experimentally determined by bringing the solution in contact with gaseous mixtures containing known and varying proportions of the gas in question. If the pressure in the solution be less than the partial pressure in the mixture, gas will be dissolved, while gas will be given off from the solution if the reverse be the case. By analyzing the gaseous mixtures, that one is found in which the gas under investigation has neither increased nor diminished, and the partial pressure of the gas in it equals the pressure of the gas in the solution.

*Oxygen.*— The proportion of oxygen in arterial blood is about 21.6 volume-per cent. That in venous blood differs in different parts of the venous system. An average of many analyses of the blood of the right heart gives its oxygen-content as 14.85 volume-per cent. As the coefficient of absorption of oxygen in water at 35°, the body temperature, is 0.0277, the maximum amount of that gas that could exist in solution in water is 2.77 volume-per cent., and it may be assumed that for simple solution the action of the blood plasma is the same as that of water. Indeed, analyses of the gases from blood-plasma and blood-serum have shown the presence of 0.26 volume-per cent. of oxygen.

It follows that almost all of the oxygen in the blood exists in some form of chemical combination in the blood-corpuscles; and we have seen that hæmoglobin is capable of forming such a combina-

tion. It has also been shown that a solution of freshly prepared, pure, crystallized oxyhæmoglobin behaves in the same manner as fresh, defibrinated blood under the influence of reduced pressures. The dissociation of oxyhæmoglobin, whether in solution or in defibrinated blood, under reduced pressures also shows, by the manner in which it takes place, that the oxygen is present in a "loose" form of chemical combination. The disengagement of oxygen does not begin immediately with reduction of pressure, indeed, this may be reduced to about half an atmosphere without any notable disengagement of oxygen. Operating at 35° to 39°, the pressure may be lowered to 410 mm. Hg without any reduction of the oxygen-content of the arterial blood, at 375 to 365 mm., it is slightly reduced, at 300 mm., the reduction is notable, and in the vacuum of the mercury pump the oxygen is completely given off.

As to the process by which the oxygen passes from the alveoli into the blood: if the oxygen pressure in the blood be less than the oxygen partial pressure in the alveoli the physical action of diffusion is sufficient to transfer the gas in the direction of the lower pressure, but if the reverse be the case some other force must be in operation. We have seen that the volume-per cent. of oxygen in alveolar air is 16, which, at 760 mm., represents a partial pressure of 121.6 mm. The oxygen pressure in arterial blood has not been determined with equal certainty. By some observers this value is given as 75 to 80 mm., but others have obtained results as high as 110 to 144 mm. The weight of evidence appears to be in favor of the lower figures, and of the consequent view that the passage of oxygen from the alveoli to the blood is a purely physical process.

*Carbon Dioxid.*—The proportion of carbon dioxid in arterial blood is 30 to 40 volume-per cent., usually nearer 40. The proportion in venous blood is about 48 volume-per cent., and in asphyxia it may rise as high as 69.21 volume-per cent. If the plasma and corpuscles be separately examined, both are found to give off carbon dioxid, and that in the relative proportion of one-third of the entire amount from the corpuscles and two-thirds from the plasma. If blood be introduced into a vacuum it bubbles and gives off all of its gas, but if blood serum or plasma be subjected to the vacuum a portion of their carbon dioxid is retained, and is only liberated upon addition of an acid. Therefore, a part of the carbon dioxid of the blood exists in the corpuscles in "loose" combination, while in the plasma a part exists in that condition, or in solution, and a part in "firm" combination; and the blood corpuscles act like the acids, in that they liberate this latter portion from its combination. Indeed oxyhæmoglobin is capable of expelling carbon dioxid from alkaline carbonates in a vacuum. Carbon dioxid apparently

exists in the corpuscles in two forms of combination. It is in part combined with hæmoglobin (p. 550), probably with its protein factor. Another portion enters into reaction with the alkaline phosphates, which are present in sufficient quantity to form alkaline bicarbonates and monophosphates.

The proportion of carbon dioxid existing in the plasma in "firm" combination has not been accurately determined. Undoubtedly it represents the alkaline carbonates resulting from decomposition of the bicarbonates (see below), but the quantity of these cannot be determined either from the quantity of carbonate left on incineration, or from the degree of alkalinity of the plasma, because the former result in part from the combustion of other organic compounds of the alkaline metals, and the latter is due in part to the presence of other alkaline compounds. Nor can the amount of carbon dioxid which is not removed by the vacuum, and only after addition of an acid, be considered as representing the whole of the firmly combined carbon dioxid, because other substances exist in the plasma, such as the globulins, which decompose a part of the alkaline carbonates in a vacuum. It can only be stated that of the 20 to 32 volume-per cent. of carbon dioxid in the plasma, from 5 to 9 volume-per cent. is retained in a vacuum, and probably represents a large part of the alkaline carbonates existing in the blood as bicarbonates. Such being the case, a notable proportion, at least, of the loosely combined carbon dioxid must exist in the plasma in the form of bicarbonates ($2NaHCO_3=Na_2CO_3+CO_2+H_2O$), from which it is liberated in vacuo by the action of weakly acid substances, such as the globulins. Indeed, the greater part of the carbon dioxid in the plasma is probably present in the form of bicarbonates, a view which is further supported by the notable diminution in the amount of carbon dioxid in the plasma in acidism (diminished alkalinity of the blood), caused either by administration of mineral acids, or by increased acid formation in diabetic coma, in which the total carbon dioxid in the plasma may fall as low as 2 to 3 volume-per cent., the excess of acid taking up the bases.

A portion of the carbon dioxid of the plasma is also in simple solution. By the method described on page 563 the carbon dioxid pressure in arterial blood has been found to be 2.8% of an atmosphere, equivalent to a pressure of 21 mm., of Hg, while in the blood of the right heart 3.81%=28.95 mm. Hg, and 5.4%=41.04 mm. Hg have been found. Comparative results between the carbon dioxid pressures in the blood and in the alveolar air are, however, not concordant. According to some observers, the blood carbon dioxid pressure is the higher, and the exit of carbon dioxid is consequently a purely physical process; while, according to others, the alveolar

partial pressure is the higher, and a "vitalistic" action of the epithelial cells is invoked to overcome the higher pressure. The oxygen entering the blood is also supposed to play a part in expelling carbon dioxid from its chemical combinations.

Tissue Respiration, or internal respiration, takes place between the blood in the capillaries and the tissues, through the lymph, and consists in the passage of oxygen from the blood to the tissues, in which the oxidations of the body occur, and the passage of the carbon dioxid and water resulting from such oxidations in the opposite direction. As oxygen enters into combination in the tissues, and is thereby removed from solution, and as carbon dioxid is there produced, it is clear that the oxygen pressure in the tissues must become less than that in the blood, while the carbon dioxid pressure in the tissues must tend to increase, and therefore the simple physical process of passage from the greater to the lesser pressure must be in operation.

## URINE.

The urine is the only pure excretion of the body, its formation has but one object, the removal of waste material, and it is the principal channel of exit from the body of water, of solid products of disassimilation, and of foreign substances, medicines, poisons, etc., more or less altered by the chemical change in the body. As the urine is obtainable without difficulty, and as it varies in composition with variations in the chemical processes of the body, analysis of the urine affords the readiest means of obtaining insight into the nature of normal chemical processes in the body, and of pathological departures therefrom. The form in which medicinal substances are eliminated in the urine is also of interest to the pharmacologist, as indicating the changes which they have undergone in their passage through the system, and their probable method of action. The toxicologist finds in the urine the last traces of poison undergoing elimination.

### PHYSICAL CHARACTERS.

Consistency.—The normal urine of man and of the carnivora is clear and transparent when voided. On standing it usually soon becomes cloudy, and a light flocculent cloud of "mucus," the "nubecula" of older authors which contains epithelium, mucus corpuscles, and urates, separates and remains suspended in the liquid. The urine of the herbivora is cloudy when voided and is alkaline in reaction, and human urine when alkaline in reaction is also cloudy. When the

urine is not perfectly transparent its cloudiness may be due to the presence of morphological elements and casts in suspension, or to the presence of phosphates or urates which have become insoluble. Phosphates thus separate from the urine when the reaction becomes subacid, and they disappear on addition of an acid. Urates are deposited from hyperacid urines and do not dissolve on addition of acid to the urine. Generally the urine has no viscidity, but alkaline urines containing pus are sometimes thick and "stringy." When shaken with air, the bubbles soon disappear from the surface of normal urine, but in urines containing sugar or bile the froth persists for quite a time. In the rare condition of chyluria, depending upon the presence of filaria in the blood, the urine is turbid and has the appearance of milk.

**Quantity.**—The average normal quantity of urine passed by an adult in 24 hours is 1,200 to 1,500 cc., being somewhat less in the female than in the male; and in children absolutely less, but relatively to weight more than in adults. The quantity is increased with increase of the amount of liquids ingested, and diminished when the secretion of perspiration is increased. **Polyuria**, i. e., increased quantity of urine, occurs pathologically in diabetes mellitus, in which it is frequently 3,000 to 5,000 cc., sometimes 10,000 to 25,000 cc., and even more, in diabetes insipidus, during absorption of large effusions, in granular atrophy of the kidneys, and in nervous diseases, such as hysteria, chorea, and epilepsy. **Oliguria**, i. e., diminished quantity of urine, occurs in continued fevers, in acute nephritis, in chronic parenchymatous nephritis, in cardiac diseases, towards the fatal termination of all diseases, in surgical shock, and under all conditions in which water is otherwise disposed of, as in diarrhœa, after hemorrhages, and during formation of dropsical effusions.

**Specific Gravity.** — The specific gravity of the mixed urine of 24 hours, when the amount is normal, is 1,015 to 1,025. The "corrected" specific gravity is the observed sp. gr., corrected to what it would be if the quantity were the normal amount of 1,200 cc., and is obtained by the formula $D=\frac{Q\times d}{1200}$, in which Q is the quantity of urine in 24 hours, and d the last two figures of the observed sp. gr. Example: $Q=600$ cc., $d=20$, then $600\times 20\div 1200=10$; sp. gr.=1,010. The sp. gr. gives a rough indication of the quantity of total solids. The last two figures of the sp. gr., multiplied by 2.33 gives, in normal urine, approximately the amount of total solids p/m. Example: sp. gr. = 1,017, $17\times 2.33=39.61$ grams of solids in 1,000 cc. This rule does not hold good if the urine contains sugar or albumin. Generally the sp. gr. varies inversely as the quantity. But in diabetes mellitus the quantity

is large and the sp. gr. high. The quantity is diminished and the sp. gr. is low in obstructive suppression, in the later stages of fatal diseases attended with defective elimination of solids, in œdema, and in diseases attended with copious diarrhœa, vomiting or sweating. For methods of determining sp. gr., see page 5.

Color.—The color of the normal urine varies from a very pale yellow to a brownish-orange, being darker when concentrated than when dilute, and also darker when strongly acid. Clinically, urines may be divided, according to color, into pale, normal, high-colored, and dark. The urine is pale when its quantity is increased. Normally-colored urines are of negative significance only. High-colored urines owe their color to the presence of the normal urinary coloring-matters in increased amount (p. 591). They occur in all forms of acute febrile disease, and indicate increased activity of tissue change. Concentrated urines are high-colored. Dark urines vary in color from orange-red to black. Exceptionally the urine may be dark from the presence of greatly increased quantity of normal coloring-matter, as in beri-beri; but usually a dark urine owes its color to the presence of an abnormal pigment: red or reddish-brown from the presence of blood-pigment; brownish-yellow, greenish-brown or dark-brown from bile coloring-matters; smoky, violet or black from derivatives of carbolic acid, resorcinol, salol, or salicylic acid; golden-yellow from santonin; yellow, changing to blood-red with alkalies, from chrysophanic acid (rhubarb, cascara, senna). In chyluria the urine is white and milky.

Odor.—When freshly voided, the odor of the urine is faint and aromatic, but on standing it rapidly develops the urinous odor, and finally that of ammonia. Certain food and medicinal substances, such as asparagus, copaiba and turpentine, communicate peculiar odors to the urine. In diabetes the urine has a faint, but distinct, "sweet" odor.

Reaction.—The reaction of the urine depends largely upon the nature of the diet. In herbivora it is neutral or alkaline; in the carnivora strongly acid. The urines of suckling herbivorous animals and that of adults during starvation, conditions in which the animals are practically carnivorous, are acid. The reaction of the normal human mixed urine of 24 hours is always acid. Samples collected at different times of the day may be normally acid, alkaline or amphoteric. After meals the acidity of human urine diminishes, and, during the period of greatest activity of stomach digestion, it may even become alkaline (p. 516). If the urine, after having been voided, is kept at the ordinary temperature, its acidity rapidly diminishes, and it becomes alkaline and ammoniacal from decomposition of the urea. It then becomes cloudy, from deposition of phosphates,

sometimes of calcium oxalate, and later of ammonium urate. The acidity of the urine may be increased by administration of dilute mineral acids, but not beyond a certain degree. It may be diminished by administration of dilute alkalies or of vegetable acids or their salts, which are oxidized in the system to carbonates. The acid reaction of the urine is due, to some extent, to the presence of carbonic acid, but principally to that of monometallic phosphates. Uric acid does not occur free, but in combination, in normal urine; therefore it does not contribute directly to the acidity, but indirectly it is largely concerned in the production of the acid reaction. The alkaline phosphates of the blood are converted into acid phosphates and urates by reaction with uric acid: $Na_2HPO_4 + C_5H_4N_4O_3 = NaH_2PO_4 + NaC_5H_3N_4O_3$; and a further formation of acid phosphate from alkaline phosphate results from the action of sulfuric acid, produced by oxidation of the sulfur of the proteins, and of hydrochloric acid reabsorbed with the peptones.

The acidity is more intense than normal in concentrated urines, in fevers, gout, acute articular rheumatism, leukæmia, scurvy, and sometimes in diabetes. The acidity of diabetic urine frequently increases after it is voided, with separation of crystals of uric acid, from the formation of acids by fermentation. The reaction may become alkaline from the presence of fixed alkalies, carbonates, or alkaline phosphates, or of volatile alkali, ammonium carbonate. Physiological subacidity or alkalinity is always due to the former, which are also the cause of the alkalinity occurring in anæmia, after cold baths, after absorption of alkaline transudates, and after administration of organic acids or mineral alkalies. Alkalinity from volatile alkali always results from decomposition of urea, which takes place in the bladder in cystitis.

The reaction of the urine has an important bearing upon the formation of calculi. Much the larger proportion of urinary calculi are either phosphatic or uric acid, and the conditions of reaction under which the two kinds are formed are the diametrical opposites; the deposition of uric acid requires a strongly acid urine, while the phosphates are deposited from subacid or alkaline urines. Uric acid calculi and "gravel" are more usually of renal origin, phosphatic calculi never. When, as frequently occurs, a uric acid calculus forms the nucleus of a large phosphatic calculus, the uric acid nucleus was formed in the kidney in a strongly acid urine, and, coming down into the bladder, has been the cause of a cystitis by mechanical irritation, which, in turn, has produced an alkaline or subacid urine, from which the phosphates have been deposited upon the uric acid nucleus.

The quality of the reaction is best determined in the usual way,

with litmus paper. If the reaction be alkaline the blued red litmus is allowed to dry in a place protected from acid fumes. If the color returns to red on drying the alkalinity is due to volatile alkali, while if the blue color persists, it is due to fixed alkali.

The determination of the degree of acidity cannot be accomplished in the usual way, by titration with standard alkaline solutions. As stated above, the acidity of the urine is due almost entirely to the presence of acid phosphates, notably of acid sodium phosphate, or monosodic phosphate, $NaH_2PO_4$. But the urine also contains disodic (and dipotassic) phosphate, $Na_2HPO_4$, whose reaction is faintly alkaline, the two salts being in varying proportion to each other. If now an alkaline solution, such as a N/10 solution of caustic soda be added to the mixture of the two salts in solution, the monosodic salt is converted into the disodic: $NaH_2PO_4+NaHO=Na_2HPO_4+H_2O$, and a time is reached when the proportion of the two is such that the reaction is not neutral, i. e., without influence upon the indicator, but amphoteric, i. e., turning red litmus blue and blue litmus red. As the measure of the degree of acidity of the urine is the amount of phosphoric acid ($P_2O_5$) present in monometallic phosphates, the determination of the acidity depends upon that of phosphoric acid in its two forms of combination, as monometallic and dimetallic salts. This is done by the Freund-Lieblein method: The total phosphoric acid (T) is first determined by the method described on p. 575. To another sample of 75 cc. of urine, 15 cc. of barium chlorid solution (100 gm. $BaCl_2.2H_2O$ to the litre) are added, by which the dimetallic phosphates (M) are precipitated, while the monometallic phosphates (D) remain in solution. The mixture is shaken, and filtered and refiltered until the filtrate is clear. Sixty cc. of the clear filtrate, representing 50 cc. of urine, are taken for a second phosphoric acid determination by the same method. As in the treatment with barium chlorid, there occurs a partial conversion of one phosphate into another, by reason of which about 3% of the phosphoric acid of the dimetallic phosphate remains in solution as monometallic salt, a correction is here necessary, and is made by subtracting 3% from the result of the second determination. The corrected result (D) represents the phosphoric acid present in monometallic phosphates.

## CHEMICAL COMPOSITION.

The constituents of the urine may be divided into two classes: normal and abnormal. Clinically some normal constituents, such as sugar, which are present in healthy urine in quantities so small as to escape detection by the tests customarily used, but are greatly increased in disease, are ranked as abnormal constituents. It is clear

that, as the normal constituents are constantly present, we can only obtain indications of clinical value by their variations in quantity. The mere presence in detectable quantity of the abnormal constituents indicates a pathological condition, the gravity of which is frequently proportionate to the quantity of the abnormal constituents voided. Quantitative determinations of both normal and abnormal constituents therefore constitute a large part of urine-analysis. As it has been found that the elimination of all constituents of the urine is subject to variation at different times of the day under different conditions of eating, sleeping, exercise, etc., quantitative results obtained with the morning urine are not comparable with those obtained from afternoon urine, indeed the only quantities which are comparable with each other are the amounts excreted in 24 hours, and no quantitative determination should be made except with samples of the mixed and measured urine of 24 hours.

The **normal constituents** of the urine are classified into the two groups of **mineral** and **organic.**

## MINERAL CONSTITUENTS.

The mineral salts are chlorids, sulfates, and phosphates of potassium, sodium, ammonium, calcium, and magnesium, with traces of silicic acid. Of the bases sodium and potassium are the most abundant, and of the acidulous factors chlorin. In the urine of 24 hours the quantity of acid present is in excess of that required to completely neutralize the amount of base present, and that, notwithstanding the fact that a portion of the bases exist in organic combinations not here considered; from which it follows that a portion of the salts must be incompletely saturated, or acid salts, such as acid sodium phosphate, $NaH_2PO_4$, and it is to these that the urine owes its acidity. It is convenient to classify the salts of the urine according to their acids, rather than according to their bases, into chlorids, sulfates and phosphates.

**Chlorids.**—The chlorids present are those of all the bases mentioned above, but sodium chlorid largely predominates, and it is usual to calculate all of the chlorin found on analysis as sodium chlorid. The usual amount of chlorids eliminated is from 10 to 15 gms. NaCl in 24 hours. It is, however, subject to great variations, chiefly due to differences in the quantity of salt taken with the food by different individuals. The elimination is less during the night than during the daytime. When NaCl is excluded from the diet its elimination by the urine ceases before it disappears from the blood. Numerous determinations of chlorids in various diseased conditions have been made, but it must be remembered that the observed departures from

the normal may be due in large part, if not entirely, to variations in the amount of salt ingested, or to removal of chlorids by other channels. The extremes of reported variations are from 0 to 50 gms. in 24 hours. Diminished elimination has been observed in acute febrile diseases, scarlatina, roseola, variola, typhus, typhoid pneumonia, yellow atrophy, in all acute renal diseases with albuminuria, in carcinoma of the stomach, gastric ulcer, anæmic conditions, rickets, melancholia, idiocy, dementia, chorea, paralysis, impetigo, pemphigus, during formation of exudates, with diarrhœa, and in chronic lead poisoning. Increased elimination occurs in acute diseases during reabsorption attended with diuresis, in diabetes insipidus, during the polyuria following attacks of epilepsy, and in general paresis when large amounts of food are taken.

The usual **methods of quantitative determination of chlorids** are by titration with silver nitrate solution, either by Mohr's or Volhard's method. The former is the most generally applicable if interfering substances be first removed. If the urine contain albumin, this is first removed by coagulation and filtration. Ten cc. of the albumin-free urine are placed in a platinum crucible along with about 1 gm. of pure (Cl-free) $Na_2CO_3$ and about 2 gm. pure $KNO_3$, and evaporated to dryness. The residue is cautiously heated to fusion, cooled, dissolved in water, and faintly acidulated with $HNO_3$. If bromids or iodids be present they must be removed at this point by adding dilute $H_2SO_4$ and a little sodium nitrite to the solution, and shaking it with successive portions of carbon disulfid until colorless. The aqueous solution is placed in a porcelain dish, with a similar dish containing an equal quantity of water alongside for comparison of tint; a few drops of neutral potassium chromate solution are added to the contents of each dish; and the silver solution is gradually added to the chlorid solution until, after stirring, it has a faint reddish tinge as compared with the contents of the second dish. The silver solution used may be either a N/10 solution, containing 17.00 gm. of pure, crystallized $AgNO_3$ to the litre, each cc. of which represents 0.00585 gm. NaCl in the 10 cc. of urine used; or a solution containing 29.054 gm. $AgNO_3$ to the litre, each cc. of which represents 0.01 gm. NaCl. The result, multiplied by 1/10 the quantity of urine in 24 hours, gives the daily elimination.

*Volhard's method* consists in precipitating the chlorids completely by an excess of silver nitrate (20 cc. of the second silver solution mentioned above) filtering, and determining the excess of silver salt in a portion of the filtrate by titration back with a solution of potassium thiocyanate containing 8.3 gm. KCNS to the litre (2 cc. of which =1 cc. $AgNO_3$ solution) using a solution of ammonio-ferric alum as an indicator, and subtracting this from the total $AgNO_3$ added.

**Sulfates.**—The sulfates of the urine, sodium and potassium sulfates, are contained only in small amount in the food; they are in great part produced in the system, as products of oxidation of the sulfur contained in the proteins. The average daily elimination is equivalent to 2.3 to 2.5 gm. of sulfuric acid ($SO_3$). The relation of nitrogen to sulfuric acid contained in the urine is quite constant at 5 N to 1 $SO_3$. Sulfuric acid exists in urine in two distinct forms of combinations: as "mineral sulfates," i. e., $K_2SO_4$, and $Na_2SO_4$, (A), and as "ether sulfates," i. e., the Na and K salts of ester-sulfuric acids corresponding in constitution to ethyl-sulfuric acid (p. 312) but containing phenolic or indolic residues (p. 589), derived from intestinal putrefaction (B). The relation between the quantities of A and B are quite variable, and the proportion of B present indicates the degree of activity of putrefactive changes in the intestine, or of retention and reabsorption of their products, in the absence of administration of phenolic compounds. Under normal conditions the relation is about A:B::10:1. The proportion of B is increased in fæcal retention, in obstructive jaundice (p. 536), and in hypochlorhydria (p. 520). In poisoning by phenols A is reduced to zero. In diarrhœa both A and B are diminished, while in acute leukæmia both are increased.

The **quantity of sulfates** is best determined gravimetrically. The total sulfates A + B, are first determined as follows: 8 cc. of strong HCl are added to 100 cc. of urine and the mixture heated to boiling. While still hot about 20 cc. of saturated $BaCl_2$ solution are added, and the mixture kept on the water-bath until the precipitate has completely subsided. The clear liquid is decanted off through a small filter, and the precipitate washed with hot water three or four times by decantation, and finally brought upon the filter and there washed, first with hot water until the washings no longer become cloudy with dilute $H_2SO_4$, then three or four times with hot, strong alcohol, and finally twice with ether. The filter and precipitate are then dried, the precipitate transferred as completely as possible to a weighed platinum crucible, the filter burnt upon the lid, the ash added to the crucible, which is then heated to moderate redness, cooled and weighed. This weight, minus that of the empty crucible, is the weight of $BaSO_4$ from 100 cc. of urine; which, multiplied by 0.34301, gives the amount of $SO_3$ in 100 cc., and this multiplied by 1/100 the quantity of urine, gives the daily elimination of total sulfuric acid ($SO_3$).

For the determination of the relation of A to B another sample of 100 cc. is mixed with 100 cc. of an alkaline solution of $BaH_2O_2$+ $BaCl_2$, which precipitates A, but not B. The mixture is stirred, allowed to settle a few minutes, and filtered through a dry filter

into a dry stoppered graduate, and the filter washed with cold water until the graduate contains 100 cc. The contents of the graduate, representing 50 cc. of urine, are transferred to a beaker, strongly acidulated with HCl, and heated to boiling, by which B is decomposed, with formation of metallic sulfates, which are then determined as above. The amount of $SO_3$ found, multiplied by $\frac{1}{50}$ the quantity of urine in 24 hours, gives the daily elimination of sulfuric acid ($SO_3$) in ester-sulfates.

**Phosphates.**—The phosphates present in the urine are those of sodium, potassium, calcium and magnesium. The Na and K phosphates are known as **alkaline phosphates** (p. 570), those of Ca and Mg as **earthy phosphates.** About two-thirds of the total phosphoric acid is contained in the alkaline phosphates, of which the sodium salt is greatly in excess of the potassium, and one-third in the earthy phosphates. The average elimination of phosphoric acid ($P_2O_5$) is 2.5 to 3 gm. per diem, but it may vary within normal limits from 1 to 5 gm. a day. This variation depends largely upon the nature of the diet, the amount being larger with an animal than with a vegetable diet. A notable quantity of phosphates are contained in food articles, both in alkaline and in earthy combination, of which the former are readily absorbed, while the latter, being soluble only in acid liquids, are in large part passed with the faeces. A part of the urinary phosphates are also formed in the system as products of oxidation of the phosphorus existing in the albumens, nucleoproteids, nucleins, protagon and the lecithins. The proportion between the amounts of nitrogen and of phosphoric acid eliminated, sometimes called the "relative value" of phosphoric acid, is calculated by the formula $N : P_2O_5 :: 100 : x$. Normally the value of $x$ is from 17 to 20; thus, taking the average elimination of nitrogen as 14 gm., and of phosphoric acid as 2.5, the value of $x$ would be 17.8. While variations in this relation depend, in some measure, upon differences in the composition of food articles ingested, they also depend upon differences in the character of tissue changes which may be experienced. The value of $x$ obtained by the above formula would be normally according as the N and $P_2O_5$ are formed by oxidation of albumens, on the one hand, or of other phosphorus-containing substances on the other.

| | N | $P_2O_5$ | $P_2O_5$ | | $x$ |
|---|---|---|---|---|---|
| [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] |
| [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] |
| [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] |
| [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] |
| [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] |
| [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] |

It is evident from the above that an increase in the relative value of phosphoric acid may be expected under conditions involving either an increased tissue change in bone, with elimination of its phosphates, or increased metabolism of tissues rich in nucleated cells. Such is the case in starvation, in which both the absolute and relative elimination of phosphoric acid, as well as that of calcium compounds, are notably increased. With increased mental activity, also, the elimination of earthy phosphates is increased, and that of alkaline phosphates diminished.

Pathologically the elimination of phosphoric acid is diminished in acute febrile diseases, chronic nephritis, amyloid degeneration of the kidney, hysteria, Addison's disease, acute yellow atrophy of the liver, and in lead poisoning. It is increased in convalescence from acute diseases, meningitis, epilepsy and leukæmia, and, particularly, in "phosphatic diabetes," in which the elimination of phosphoric acid may reach 8 to 9 gm. in 24 hours, and in which the other symptoms of diabetes are present, but there is no glycosuria. In diabetes mellitus the quantity of phosphoric acid is subnormal, particularly when the quantity of sugar is large.

The earthy phosphates only are concerned in the formation of calculi. So long as the reaction of the urine (p. 569) remains acid they are held in solution, but when the reaction becomes alkaline, or even on loss of $CO_2$ on exposure to air, the insoluble trimetallic salts are formed and deposited. Alkaline urines are, for this reason, almost always turbid, and become clear upon addition of an acid. It is in such urine that **phosphatic calculi** are always formed, usually about a nucleus of uric acid, or of a foreign body. If the alkalinity be due to the formation of ammonia, the **ammonio-magnesium phosphate**, or **triple phosphate**, $Mg(NH_4)PO_4$, is produced, either in the form of large, tubular crystals, or as a **fusible calculus.**

A process for the **quantitative determination of phosphoric acid** in the urine is based upon the formation of the insoluble uranium phosphate, and upon the production of a brown color when a solution of a uranium salt is brought in contact with a solution of potassium ferrocyanid. Four solutions are required: (1) *a standard solution of disodic phosphate*, made by dissolving 10.085 grams of crystallized, non-effloresced $HNa_2PO_4$ in $H_2O$, and diluting to a litre; (2) *an acid solution of sodium acetate*, made by dissolving 100 grams sodium acetate in $H_2O$, adding 100 cc. glacial acetic acid, and diluting with $H_2O$ to a litre; (3) *a strong solution of potassium ferrocyanid*; (4) *a standard solution of uranium acetate*, made by dissolving 20.3 grams of yellow uranic oxid in glacial acetic acid, and diluting with $H_2O$ to nearly a litre. Solution 1 serves to determine the true strength of this solution, as follows: 50 cc. of Solution 1 are placed in a beaker, 5 cc.

of Solution 2 are added, the mixture heated on a water-bath, and the uranium solution gradually added, from a burette, until a drop from the beaker produces a brown color when brought in contact with a drop of the ferrocyanid solution. At this point the reading of the burette, which indicates the number of cc. of the uranium solution, corresponding to 0.1 —$P_2O_5$, is taken. A quantity of $H_2O$, determined by calculation from the result thus obtained, is then added to the remaining uranium solution, such as to render each cc. equivalent to 0.005 gram $P_2O_5$.

To determine the total phosphates in a urine: 50 cc. are placed in a beaker, 5 cc. sodium acetate solution are added; the mixture is heated on the water-bath, and the uranium solution delivered from a burette, until a drop, removed from the beaker and brought in contact with a drop of ferrocyanid solution, produces a brown tinge. The burette reading, multiplied by 0.005, gives the amount of $P_2O_5$ in 50 cc. urine; and this, multiplied by $\frac{1}{50}$ the amount of urine passed in 24 hours, gives the daily elimination.

To determine the *earthy phosphates*, a sample of 100 cc. urine is rendered alkaline with $NH_4HO$, and set aside for 12 hours. The precipitate is then collected upon a filter, washed with ammoniacal water, brought into a beaker, dissolved in a small quantity of acetic acid; the solution diluted to 50 cc. with $H_2O$, treated with 5 cc. sodium acetate solution, and the amount of $P_2O_5$ determined as above.

**Metallic Elements.**—The metallic elements of urinary salts are sodium, potassium, calcium, and magnesium. Sodium and potassium are present, not only in combination with mineral acids, but also in organic combination, as in the urates. The daily elimination is equal to 2–3 gm. $K_2O$, and 4–6 gm. $Na_2O$; or K:Na::2.5:5. Calcium and magnesium are present principally in their phosphates, in less amount as chlorids, and occasionally their urates are met with in calculi. About 1 gm. of Ca and Mg is eliminated in 24 hours, in the proportion of 2/3 Mg and 1/3 Ca.

## NORMAL ORGANIC CONSTITUENTS OF THE URINE.

Urea — Carbamid — $H_2N$–CO–$NH_2$ — (p. 348) — is the most abundant of the organic constituents of the urine, and is the chief end-product of the metabolism of the proteins of the body. Normally, in the urine of adults 84 to 91%, and in that of infants 73 to 76% of the total nitrogen of the urine is contained in urea, the remainder entering into the composition of creatinin, uric acid, xanthin bases, ammoniacal compounds, carbamates, hippuric acid, indoxyl- and skatoxyl-sulfates and, exceptionally, of allantoïn, leucin and tyrosin.

It is highly improbable that urea is formed by any simple transition from protein substances in the body. Indeed it is doubtful whether it can be produced from protein material outside of the body by a single reaction. It is derived from both the "circulating" proteins, i. e., those contained in the blood and lymph, and the "tissue" proteins, i. e., those which exist in the tissues, and, as these include almost all of the animal proteins, differing from each other notably in structure, it is probable that urea is produced in the system by more than one, and probably by several, series of reactions.

The formation of urea from ammonium carbonate, and from other ammoniacal salts convertible into the carbonate, is a simple dehydration: $O:C\begin{matrix}O.NH_4\\O.NH_4\end{matrix} - 2H_2O = O:C\begin{matrix}NH_2\\NH_2\end{matrix}$, which is readily effected outside of the body, and which has been shown to take place in the liver. This method of production of urea, and this seat of its formation, are the only ones which have been positively demonstrated, but the ammoniacal compounds are far removed from the proteins in the scale of decomposition, and it is not presumable that urea is formed in the liver exclusively.

Another direct progenitor of urea by simple dehydration is ammonium carbamate: $O:C\begin{matrix}NH_2\\O.NH_4\end{matrix} - H_2O = O:C\begin{matrix}NH_2\\NH_2\end{matrix}$, which has been found to be a constant constituent of the blood and urine, and to be greatly increased in the latter after the ingestion of large quantities of calcic hydroxid. In support of the view that ammonium carbamate is converted into urea, or, at all events, into some other substance, in the liver, it is stated that in dogs in which the portal vein has been made to empty directly into the vena cava, the administration of ammonium carbamate produces symptoms of carbamate poisoning, which are not observed when the same salt is administered to animals not so operated upon.

Carbamic acid is amido-formic acid (p. 346), the first term of series of mono-amido-fatty acids. Other amido-acids of the same series, such as glycocoll and leucin, and of the succinic series, as aspartic acid, are also undoubtedly intermediate products in the formation of urea. On oxidation in alkaline solution these substances yield carbamic acid, and, on the other hand, they are constant products of decomposition of albumens by the action of oxidizing agents, or of mineral acids, as well as by that of proteolytic enzymes (p. 499), but to what extent they are thus formed in the system is undetermined. It cannot be doubted, however, that the amido-acids are decomposed, with formation of urea, probably with ammonium carbamate as an intermediate product, and that such formation takes place to a notable extent in the liver.

It has been shown that glycocoll, leucin and aspartic acid, contained in arterial blood, which is made to traverse the isolated livers of dogs, are converted into urea or into some substance closely related to it. Another fact in support of the view that urea is produced from leucin in the liver is that, while this amido-acid is not found in normal urine, it makes its appearance there in notable quantity, while the proportion of urea is correspondingly diminished, in yellow atrophy and in acute phosphorus poisoning, in both of which conditions the function of that organ is seriously interfered with.

Another method of formation of urea is through creatin (p. 336), which is known to be a product of the metabolism of muscular tissue, and through the allied hexon bases, lysatin, arginin, etc., which are products of the tryptic digestion of proteins, and which yield urea under the influence of hydrolyzing agents (p. 499). Creatin is methyl-guanidin acetic acid (p. 336), and, by hydrolysis it readily yields sarcosin, or methyl-glycocoll, and urea: $HN{:}C\begin{smallmatrix}\diagup NH_2\\ \diagdown N-CH_3\end{smallmatrix}\!\!\diagup CH_2.COOH + H_2O = HN\begin{smallmatrix}\diagup CH_2.COOH\\ \diagdown CH_3\end{smallmatrix} + H_2N.CO.NH_2$. It must be admitted, however, that sarcosin is not known to exist in the body in its own form, and that a large part, at least, of the creatin formed in the system is eliminated as creatinin (p. 585).

Chemically a logical method of formation of urea is that from the nucleoproteids, through the xanthin bases and uric acid by progressive oxidation (p. 356). That the nucleoproteids yield nucleins, and that the purin bases, including uric acid, are derived from these cannot be doubted, but the formation of urea from uric acid in the system has been questioned, and even denied. Yet it is highly probable that such formation does take place. The constitution of uric acid and the methods of its synthesis, notably that from urea and glycocoll (p. 358) indicate that by hydrolysis it should produce urea and a monureid (p. 351), and this reaction does occur outside of the body, as when uric acid is decomposed into urea and alloxan by hydrolytic oxidation: $C_5H_4N_4O_3 + H_2O + O = CON_2H_4 + C_4H_2N_2O_4$. It has also been shown experimentally that uric acid administered to animals is in large part eliminated as urea.

The quantitative relations of the several nitrogenous constituents of the urine vary greatly under different conditions, normal and pathological. Thus the amount of uric acid normally varies from 1/35 to 1/60 of the amount of urea, and, as stated above, under pathological conditions, urea is to a great extent replaced by leucin and tyrosin, which are not present in normal urine. The observed variations in the proportion of the amount of nitrogen contained in the urea to the total nitrogen, have extended from 50 to 90%.

Although countless so-called quantitative determinations of urea have been made, very little is known of the actual quantities of urea present in the urine under different conditions of health and disease. This is because almost all of the processes used, and all of those in general use, include in their results, not only urea, but all the nitrogen of the creatinin and a part of that of the uric acid, calculated as urea. Nor do the results of these methods indicate the total nitrogen. Therefore in the statements below, relating to the "quantity of urea," that expression must be considered as referring to this large fraction of the total nitrogen, including all of that contained in urea, calculated as urea.

In the present condition of our knowledge more valuable results are to be expected from determinations of total nitrogen (by the Kjeldahl method) than from determinations of urea, either absolute or in the sense as above limited. The quantity of nitrogen in various food articles can be obtained from König's tables, and from these figures the quantity of nitrogen ingested in a weighed dietary can be calculated. On the other hand, determinations of the total nitrogen in fæces and urine for the same period will give the amount of nitrogen eliminated. When these two quantities equal each other the system is said to be in a condition of "nitrogenous equilibrium," a condition which is approximately fulfilled in health. But if the amount of nitrogen eliminated exceeds that ingested, the excess has its origin in abnormal protein metabolism. But little has as yet been accomplished along this line. The results are best expressed as nitrogen, not either as urea, or, as has been proposed, in terms of the amount of nitrogen contained in lean meat (3.4%). The normal elimination of nitrogen is from 10 to 16 gm., equivalent to 21.4 to 34.3 gm. urea. As 60 parts of urea contain 28 parts by weight of nitrogen: urea $\times 0.467$=nitrogen; and nitrogen $\times 2.143$=urea.

The **quantity of urea** eliminated in 24 hours is subject to normal variations according to age, sex, diet, and exercise: In new-born children the elimination of urea is insignificant. By growing children the amount voided is absolutely less than that discharged by adults, but, relatively to their weight, considerably greater; thus, Harley gives the following amounts of urea in grams for each pound of body-weight in twenty-four hours: Boy, eighteen months, 0.4; girl, eighteen months, 0.35; man, twenty-seven years, 0.25; woman, twenty-seven years, 0.20. During adult life the mean elimination of urea remains stationary, unless modified by other causes than age. In old age the amount sinks to below the absolute quantity discharged by growing children.

At all periods of life females eliminate less urea than males. The proportion given by Beigel differs slightly from that of Harley,

viz.: one kilo of male, 0.35 gram urea in twenty-four hours; one kilo of female, 0.25 gram. During pregnancy females discharge more urea than males; but very shortly after delivery the amount sinks to the normal, below which it passes during lactation.

The quantity of urea eliminated is in direct proportion to the amount of nitrogen contained in the food. The ingestion of large quantities of watery drinks increases the amount, and a contrary effect is produced by tea, coffee, and alcohol. With insufficient food the excretion of urea is diminished, although not arrested, even in extreme starvation.

The question whether the elimination of urea is increased during violent muscular exercise is one which has been the subject of many observations and of much discussion. An examination of the various results shows that, while the excretion of urea is slightly greater during violent exercise than during periods of rest, the increase is so insignificant in comparison to the work done, and, in some instances, to the loss of body-weight, as to render the assumption that muscular force is the result of the oxidation of the nitrogenized constituents of muscle improbable. (See Gamgee, "Physiological Chemistry," I, pp. 385–401, for a full review of the subject.)

The percentage of urea in the urine of the same individual is not the same at different times of the day. The minimum hourly elimination is in the morning hours; an increase begins immediately after the principal meal, and reaches its height in about six hours, when a diminution sets in and progresses to the time of the next meal. Gorup-Besanez gives a curve representing the hourly variations in the elimination of urea, which, reduced to figures, gives the following:

| Hour. | Urea in Grams. | Hour. | Urea in Grams. | Hour. | Urea in Grams. |
|---|---|---|---|---|---|
| 8– 9 A. M. . . . . | 1.5 | 4– 5 P. M. . . . | 2.6 | 12–1 A. M. . . . | 1.9 |
| 9–10 A. M. . . . . | 1.5 | 5– 6 P. M. . . . | 3.1 | 1–2 A. M. . . . | 1.9 |
| 10–11 A. M. . . . . | 1.4 | 6– 7 P. M. . . . | 2.8 | 2–3 A. M. . . . | 1.9 |
| 11 A. M.–12 M. . . . | 1.3 | 7– 8 P. M. . . . | 2.5 | 3–4 A. M. . . . | 1.8 |
| 12 M.–1 P. M. . . . | 1.8 | 8– 9 P. M. . . . | 2.3 | 4–5 A. M. . . . | 1.6 |
| 1–2 P. M. . . . . | 1.9 | 9–10 P. M. . . . | 2.0 | 5–6 A. M. . . . | 1.6 |
| 2–3 P. M. . . . . | 2.1 | 10–11 P. M. . . . | 2.0 | 6–7 A. M. . . . | 1.6 |
| 3–4 P. M. . . . . | 2.3 | 11–12 P. M. . . . | 2.3 | 7–8 A. M. . . . | 1.5 |

The total of which, however, represents a quantity above the normal.

The absolute amount of urea eliminated in twenty-four hours is increased by the exhibition of diuretics, alkalies, colchicum, turpentine, rhubarb, alkaline silicates, and compounds of antimony,

arsenic, and phosphorus. It is diminished by digitalis, caffein, potassium iodid, and lead acetate; not sensibly affected by quinin.

In acute febrile diseases both the relative and absolute amounts of urea eliminated augment, with some oscillations, until the fever is at its height. There is, however, no constant relation between the amount of urea eliminated and the body temperature. During the period of defervescence, the amount of urea eliminated in twenty-four hours is diminished below the normal; during convalescence it again slowly increases. If the malady terminate in death the diminution of urea is continuous to the end. In intermittent fever the amount of urea discharged is increased on the day of the fever and diminished during the interval. In cholera, during the algid stage, the elimination of urea by the kidneys is almost completely arrested, while the quantity in the blood is greatly increased. When the secretion of urine is again established, the excretion of urea is greatly increased (60–80 grams a day), and the abundant perspiration is also rich in urea. In cardiac diseases, attended with respiratory difficulty, but without albuminuria, the elimination of urea is diminished and that of uric acid increased. In nephritis, attended with albuminuria, the elimination of urea at first remains normal; later it diminishes, and the urea, accumulating in the blood, has been considered by many as the cause of uræmic poisoning. It appears more probable, however, that the symptoms of uræmia are due to the retention in the blood of alkaloidal poisons normally excreted in small amount. The quantity of urea in the urine is also diminished in all diseases attended with dropsical effusions; but is increased when the dropsical fluid is reabsorbed. In true diabetes the amount of urea in the urine of twenty-four hours is greater than normal. In chronic diseases the elimination of urea is below the normal, owing to imperfect oxidation.

To detect the presence of urea in a fluid, it is mixed with three to four volumes of alcohol, and filtered, after having stood several hours in the cold; the filtrate is evaporated on the water-bath, and the residue extracted with strong alcohol; the filtered alcoholic fluid is evaporated, and the residue tested as follows:

(1) A small portion is heated in a dry test-tube to about 160° (320° F.), until the odor of ammonia is no longer observed; the residue is treated with a few drops of caustic potassa solution and one drop of cupric sulfate solution. If urea be present, the biuret resulting from its decomposition by heat causes the solution of the cupric oxid with a reddish-violet color. The same appearance is produced in solutions containing peptone (Biuret test).

(2) A portion of the residue is dissolved in a drop or two of $H_2O$, and an equal quantity of *colorless* concentrated $HNO_3$ added; if

urea be present in sufficient quantity there appear white, shining, hexagonal or rhombic, crystalline plates or six-sided prisms of urea nitrate (Fig. 38).

(3) A portion dissolved in water, as in (2) is treated with a solution of oxalic acid; rhombic plates of urea oxalate crystallize.

**Determination of Quantity of Urea in Urine.**—It must not be forgotten that, in all quantitative determinations of constituents of the urine, the question to be solved is not how much of that constituent is contained in a given quantity of urine, but how much of that substance the patient is discharging in a given time, usually twenty-four hours. Quantitative determinations are, therefore, in most cases, barren of useful results, unless the quantity of urine passed by the patient in twenty-four hours is known; and, in view of diurnal variations in elimination, unless the urine examined be a sample taken from the *mixed urine of twenty-four hours*.

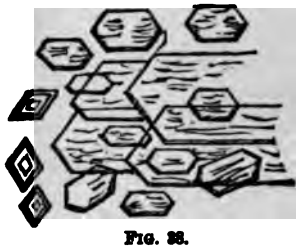


FIG. 38.

The process giving the most accurate results is that of Bunsen, in which the urea is decomposed into $CO_2$ and $NH_3$, the former of which is weighed as barium carbonate. Unfortunately, this process requires an expenditure of time and a degree of skill in manipulation which render its application possible only in a well-appointed laboratory.

A process which is described in most text-books upon urinary analysis, and which is much used by physicians, is that of Liebig. As this method is one, however, which contains more sources of error than any other, and as it can only be made to yield approximately correct results by a very careful elimination, as far as possible, of those defects, it is not one which is adapted to the use of the physician.

Probably the most satisfactory process in the hands of the practitioner is that of Hüfner, based upon the reaction, to which attention was first called by Knop, of the alkaline hypobromites upon urea (p. 349); using, however, Dietrich's apparatus, or the more simple modification suggested by Rumpf, in place of that of Hüfner. The apparatus (Fig. 39) consists of a burette of 30–50 cc. capacity, immersed in a tall glass cylinder filled with water, and supported in such a way as to admit of being raised or lowered at pleasure. The upper end of the burette communicates with the evolution bottle *a*, which has a capacity of 75 cc., by means of a rubber tube.

The reagent required is made as follows: 27 cc. of a solution of caustic soda, made by dissolving 100 grams NaHO in 250 cc. $H_2O$, are brought into a stoppered, graduated cylinder, 2.5 cc. bromin

are added, the mixture shaken, and diluted with water to 150 cc. The caustic soda solution may be kept in a bottle having a rubber stopper, but the mixture must be made up as required, a fact which, owing to the irritating character of the bromin vapor, renders the use of this reagent in a physician's office somewhat troublesome. The bromin is best measured by a pipette of suitable size, having a compressible rubber ball at the upper end.

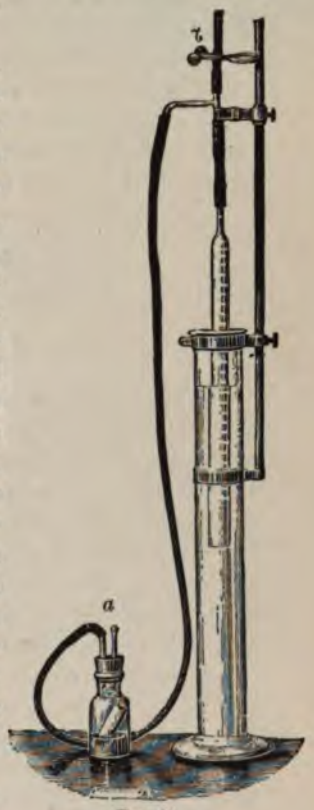


FIG. 39.

To conduct a determination, about 20 cc. of the hypobromite solution are placed in the bottle *a*; 5 cc. of the urine to be examined are placed in the short test-tube, which is then introduced into the position shown in the figure, care being had that no urine escapes. The cork, with its fittings, is then introduced, the pinchcock *b* opened, and closed again when the level of liquid in the burette is the same as that in the cylinder. The decomposing vessel *a* is then inclined so that the urine and hypobromite solution mix; the decomposition begins at once, and the evolved N passes into the burette, which is raised from time to time, so as to keep the external and internal levels of water about equal; the $CO_2$ formed is retained by the soda solution. In about half an hour (the decomposition is usually complete in ten minutes, but it is well to wait half an hour) the height is so adjusted that the inner and outer levels of water are exactly even, and the graduation is read, while the standing of the barometer and thermometer are noted at the same time.

In calculating the percentage of urea from the volume of N obtained, it is essential that a correction should be made for differences of temperature and pressure, without which the result from an ordinary sample of urine may be vitiated by an error of 10 per cent. If, however, the temperature and barometric pressure have been noted, the correction is readily made by the use of the table (see Appendix B, III), computed by Dietrich, giving the weight of 1 cc. N at different temperatures and pressures.

In the square of the table in which the horizontal line of the observed temperature crosses the vertical line of the observed barometric pressure will be found the weight, in milligrams, of a cc.

of N; this, multiplied by the observed volume of N, gives the weight of N produced by the decomposition of the urea contained in 5 cc. urine. But as 60 parts urea yield 28 parts N, the weight of N, multiplied by 2.143, gives the weight of urea in milligrams in 5 cc. urine. This quantity, multiplied by twice the amount of urine in 24 hours, and divided by 10,000, gives the amount of urea eliminated in 24 hours in grams. If the result be desired in grains the amount in grams is multiplied by 15.432.

*Example.*—Five cc. urine decomposed; barometer = 736 mm.; thermometer = 10°; burette reading before decomposition = 64.2; same after decomposition = 32.6; cc. N collected = 31.6. From the table 1 cc. N at 10° and 736 mm. BP weighs 1.1593. The patient passes 1500 cc. urine in 24 hours:

$$31.6 \times 1.1593 = 36.6339 = \text{milligr. N in 5 cc. urine.}$$
$$36.6339 \times 2.14 = 78.3965 = \text{milligr. urea in 5 cc. urine.}$$
$$\frac{78.3965 \times 3000}{10{,}000} = 23.519 = \text{grams urea in 24 hours.}$$
$$23.519 \times 15.432 = 362.94 = \text{grains urea in 24 hours.}$$

In using this process it is well to have the urea solution as near the strength of one per cent. as possible; therefore if the urine be concentrated, it should be diluted. Even when carefully conducted, the process is not strictly accurate; creatinin and uric acid are also decomposed with liberation of N, thus causing a slight plus error; on the other hand, a minus error is caused by the fact that in the decomposition of urea by the hypobromite, the theoretical result is never obtained within about eight per cent. in urine. These errors may be rectified to a great extent by multiplying the result by 1.044.

A process which does not yield as accurate results as the preceding, but which is more easy of application, is that of Fowler, based upon the loss of sp. gr. of the urine after the decomposition of its urea by hypochlorite. To apply this method the sp. gr. of the urine is carefully determined, as well as that of the liq. sodæ chlorinatæ (Squibb's). One volume of the urine is then mixed with exactly seven volumes of the liq. sod. chlor., and, after the first violence of the reaction has subsided, the mixture is shaken from time to time during an hour, when the decomposition is complete; the sp. gr. of the mixture is then determined. As the reaction begins instantaneously when the urine and reagent are mixed, the sp. gr. of the mixture must be calculated by adding together once the sp. gr. of the urine and seven times the sp. gr. of the liq. sod. chlor., and dividing the sum by 8. From the quotient so obtained the sp. gr. of the mixture after decomposition is subtracted; every degree of loss in sp. gr. indicates 0.7791 gram of urea in 100 cc. of urine. The sp.

gr. determinations must all be made at the same temperature; and that of the mixture only when the evolution of gas has ceased entirely.

Finally, when it is only desired to determine whether the urea is greatly in excess or much below the normal, advantage may be taken of the formation of crystals of urea nitrate. Two samples of the urine are taken, one of 5 drops and one of 10 drops; the latter is evaporated, at a low temperature, to the bulk of the former, and cooled; to each, three drops of colorless $HNO_3$ are added. If crystals do not form within a few moments in the concentrated sample, the quantity of urea is below the normal; if they do in the unconcentrated sample, it is in excess. In using this very rough method, regard must be had to the quantity of urine passed in 24 hours; the above applies to the normal amount of 1200 cc.; if the quantity be greater or less, the urine must be concentrated or diluted in proportion. The *amorphous* white ppt. caused by $HNO_3$ in albuminous urine must not be mistaken for the *crystalline* deposit of urea nitrate.

For the **determination of total nitrogen** 5 cc. of urine are placed in a long-necked Kjeldahl digesting flask along with 0.5 gm. of $CuSO_4$ and 15 cc. of concentrated $H_2SO_4$. The flask is supported at 45° to the horizontal and gradually heated until white fumes are given off; 10 gm. of $K_2SO_4$ are then added, and the contents of the flask heated just short of boiling until almost colorless. After cooling, the contents of the digesting flask are transferred and washed into a distilling flask; the acid is nearly neutralized by the slow addition of NaHO solution (sp. gr. 1.24); a few pieces of granulated zinc are added, and then a moderate excess of NaHO solution, whereupon the flask is immediately connected with a bulb tube and condenser, so arranged as to deliver the distillate into a recipient containing 30 cc. of N/5 $H_2SO_4$ and a little lacmoid as an indicator. The distillation is continued until about 2/3 of the liquid have passed over, when the excess of $H_2SO_4$ remaining in the recipient is determined by titration with N/5 NaHO solution. Each cc. of N/5 acid neutralized by the ammonia formed in the process corresponds to 0.0028 gm. of nitrogen in the 5 cc. of urine used. A blank process must be conducted with reagents alone to guard against error from nitrogen compounds in the reagents or in the air.

**Creatinin** — (p. 336) is the lactam of creatin, or methylguanidin acetic acid, from which it is derived in the body by dehydration: $HN{:}C\begin{smallmatrix}\diagup NH_2 \\ \\ \diagdown N{-}CH_3\end{smallmatrix}\!\!\diagup CH_2.COOH - H_2O = HN{:}C\begin{smallmatrix}\diagup NH.CO \\ \\ \diagdown N{-}CH_3\end{smallmatrix}\!\!\diagup CH_2$, and exists in the blood and urine of adults, and in traces in milk, although it is

absent in the urine of nursing infants. The quantity eliminated is slightly greater than that of uric acid, 1.7 to 2.1 gm. in 24 hours. It appears to follow the same variations as urea, and to be formed in slightly greater amount with increased muscular activity. But little is known of its pathological variations, except that it is diminished in amount in progressive muscular atrophy, in other diseases of the muscles, and in paralyses.

It is quantitatively determined as its zinc chlorid compound: 240 cc. of the urine, freed from albumin and sugar, if present, by coagulation and fermentation, are placed in a 300 cc. cylinder, rendered alkaline with milk of lime, precipitated with $CaCl_2$ solution, made up to 300 cc., mixed and filtered. Of the filtrate 250 cc. (= 200 cc. urine) are acidulated with acetic acid, and evaporated to 20 cc. The residue is mixed with absolute alcohol, the solution made up to 100 cc., allowed to stand 24 hours and filtered. Of the filtrate 80 cc. (= 160 cc. urine) are placed in a beaker with 1 cc. of an acid-free solution of zinc chlorid, sp. gr. 1.2, and allowed to stand, covered, in a cool place for two days. The crystalline zinc-creatinin compound is collected on a small, weighed filter, washed with a little alcohol until the washings are free from chlorin, dried at 110° and weighed. The weight obtained, minus that of the filter, multiplied by 0.648 gives the weight of creatinin in 160 cc. urine. If the deposit contains sodium chlorid, recognizable by the cubical shape of the crystals, it is treated with $HNO_3$, which is then evaporated, and the residue of zinc oxid is ignited, washed with water, dried and weighed. The weight of the zinc oxid obtained by 2 gives the weight of creatinin.

[illegible]

notably with the diet, and in the same manner as urea. With a mixed diet the average daily elimination is 0.7 gm.; with a vegetable diet it may fall as low as 0.3 gm., and with a surfeit of animal food it may rise as high as 1.5 to 2.00 gm. There is also an hourly variation, the maximum elimination occurring two to five hours after the principal meal, and the minimum is thirteen hours after. The normal relation of uric acid to urea varies from 1:50 to 1:70.

The results of quantitative determinations in pathological conditions are somewhat conflicting, and those obtained by the older methods are for the most part erroneous, being affected with a minus error. The following facts may, however, be considered as established: In leukæmia there is both absolute and relative increase, the absolute amount being from 1 to 5 gm. in 24 hours, and the proportion to urea increased to 1:45 to 1:12. A similar increase occurs in splenic diseases, and in hepatic cirrhosis. In gout there is diminished elimination during the chronic period, most marked just preceding an attack, and an increased elimination during and following the exacerbations. In acute articular rheumatism the elimination increases, to return to and fall below the normal during convalescence. In diabetes the amount of uric acid is usually subnormal, although it is often increased to as high as 3 gm. in 24 hours, when the sugar is diminished in quantity. By reason of its very sparing solubility, uric acid frequently forms sediments and calculi, consisting either of free uric acid or of the less soluble of the urates. It must be noted in this connection that uric acid is much more soluble in the presence of urea than in pure water. While 15,000 parts of water are required to dissolve 1 part of uric acid, the same quantity dissolves in 1900 parts of a 2% solution of urea, about the proportion contained in the urine.

The principal **methods of quantitative determination** of uric acid are those of Heintz, of Hopkins and the Ludwig-Salkowski method. The older *method of Heintz*, which consists in precipitation of the uric acid by strong acidulation with hydrochloric acid, and weighing the crystals, is frequently inaccurate by reason of incomplete precipitation by this treatment; indeed, samples are met with from which no precipitation whatever occurs.

*Hopkins' method* is but slightly more elaborate than Heintz's, but much more reliable: 100 cc. of urine are saturated with powdered ammonium chlorid (for which about 30 gm. are required), and the solution mixed and allowed to stand 2 to 3 hours with occasional stirring. By this treatment the uric acid is almost completely precipitated as acid ammonium urate. The precipitate is collected on a filter, washed with saturated $NH_4Cl$ solution, and dissolved in the smallest possible quantity of hot water. To this solution 5 cc. of

HCl (1:3) are added, and the mixture evaporated on the water bath until crystals of uric acid begin to form. These are collected upon a small, weighed filter, washed successively with water, alcohol and ether, dried and weighed. A correction is necessary for the slight solubility of uric acid, which is made by adding 0.045 mgm. for each cc. of water used in the final washing.

The *Ludwig-Salkowski method* is more accurate, but more intricate, and requires to be rapidly conducted to avoid error. It depends upon the precipitation of the uric acid as its silver salt, the decomposition of this by HCl, and the collection and weighing of the liberated uric acid. The student is referred to more comprehensive treatises for the details of the process.

It has been recommended to dissolve the precipitated uric acid in the Hopkins and Ludwig-Salkowski methods in alkali and to titrate the solution with potassium permanganate. This does not materially abbreviate the processes, and adds further sources of error.

**Xanthin Bases**—(p. 356).—The occurrence of guanin and of carnin in the urine has not been demonstrated; and of the remaining xanthin bases which are met with in the urine the most abundant are heteroxanthin, paraxanthin, and 1-monomethyl-xanthin. They are normally present in small amount only, the total elimination being from 15 to 45 mgm. in 24 hours. They undoubtedly originate in the metabolism of the nucleoproteids, and are increased in amount after administration of nucleins, and in conditions attended with increased metabolism of leucocytes. They may also originate from the caffein and theobromin contained in coffee, tea and cocoa (p. 358). Xanthin occasionally forms vesical calculi of considerable size. Their quantitative determination is best effected by Salkowski's method, based upon precipitation of their silver compounds.

**Hippuric Acid**—(p. 425)—is an aromatic amido-acid, benzoyl-amido acetic acid, which exists in greatest abundance in the urine of the herbivora, and only in small amount in normal human urine, although the daily elimination varies within quite wide limits, 0.29 to 2.84 gm., and is still further increased when benzoic acid, cinnamic acid or substances containing those acids or their compounds are taken.

Hippuric acid may be considered as formed by the substitution of the radical, benzoyl, of benzoic acid for a hydrogen atom in the amido group of amido-acetic acid: $C_6H_5.CO.OH+CH_2.NH_2.COOH=H_2O+CH_2.NH(C_6H_5.CO).COOH$; its production in the body, therefore, involves the formation of glycocoll and of an aromatic derivative which may supply the benzoyl factor. Both of the constituents of hippuric acid result, undoubtedly, from protein metabolism. Gly-

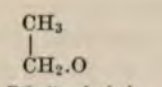
cocoll is a well-recognized product of such action, but the method and seat of production of the benzoyl radical are not so clear. Benzoyl-propionic acid, $CH_2(C_6H_5,CO).CH_2.COOH$, is known to be a product of intestinal putrefaction; and that this is capable of yielding the benzoyl radical is demonstrated by the fact that when it is injected into the circulation it is eliminated as hippuric acid. The administration of benzoic acid is also followed by a corresponding increase in the elimination of hippuric acid. That some of the steps in the formation of hippuric acid are the result of intestinal putrefaction is also indicated by marked diminution in its elimination in dogs whose intestines are disinfected. It is possible, also, that the final steps may occur in the kidney, as hippuric acid is formed when arterial blood containing glycocoll and benzoic acid is passed through the isolated kidneys of dogs.

Little is known of the variations in elimination of hippuric acid in pathological conditions.

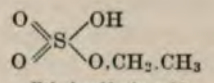
**Oxaluric Acid**—(p. 352)—is a monureid, $(CON_2H_3)CO.COOH$, which exists in the urine as its ammonium salt in very small amount. It is readily decomposed, even by boiling its solution, into urea and oxalic acid, and it is undoubtedly concerned in the formation of the oxalates of the urine.

**Allantoïn**—(p. 353)—is a diureid which occurs in very minute quantity in the urine of adults, in somewhat larger amount in that of pregnant women, and in that of infants during the first eight days of life, when the quantity of urea is very small. It is increased in the urine of dogs after administration of uric acid, and is, possibly, produced from this in the economy.

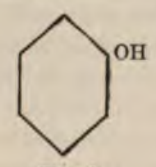
**Ester-sulfates.**—The occurrence of these compounds has been referred to in connection with the sulfates (p. 573), and they are considered here at greater length, as the most important among them contain nitrogen. Their constitution is similar to that of the acid esters (p. 311), from which they differ in containing phenolic in place of alcoholic radicals. Their relations are shown by the following formulæ:



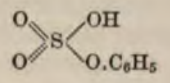
Ethylic alcohol.



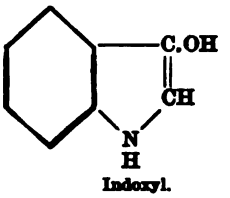
Ethyl-sulfuric acid.



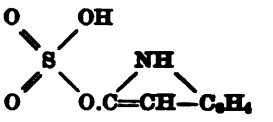
Phenol.



Phenyl-sulfuric acid.




Indoxyl.




Indoxyl-sulfuric acid.

The compounds of this class which are known to occur in the urine are the sodium and potassium salts, particularly the latter, of the ester-sulfuric acids of phenol, para-cresol, catechol, quinol, indoxyl, and skatoxyl.

The phenol and para-cresol compounds are usually determined together by precipitation with bromin water, by a method which is not very accurate, and which determines not only the phenols in this form of combination, but also that existing in phenyl-glucuronic acid. By this method the amount of phenol and para-cresol eliminated has been found to vary from 17 to 51 mgm. in 24 hours. They vary inversely as the mineral sulfates (p. 573), at whose expense they are formed. They have not the poisonous qualities of the phenols from which they are derived, and their formation serves to protect the system not only from the toxic effects of these substances, when formed as products of intestinal putrefaction, but also from that of carbolic acid to the limit of the amount of sulfates available. In poisoning by carbolic acid the whole of the sulfuric acid of the urine is in ethereal combination.

Of the three diphenols, catechol and quinol have been found in the urine of the horse, and in traces in human urine. The third, resorcinol, has not been met with in this situation.

Indoxyl-sulfates—Indican—Uroxanthin—(p. 465) is the principal parent substance of urinary indigo, which is also derived from indoxyl-glucuronic acid. The origin of both is undoubtedly in the indole produced in intestinal putrefaction. They disappear from the urine of dogs whose intestines are disinfected, they are not present in the urine of new-born infants, and they were also absent in a case of artificial anus at the lower part of the ileum.

The amount of indigo derivable from the two compounds mentioned, eliminated in 24 hours, is from 5 to 20 mgm. normally in man. In some of the lower animals it is much greater, in the horse 25 times greater. It is nearer the higher limit with animal food, nearer the lower with a vegetable diet. The elimination of an excess is designated as indicanuria, and is a measure of the intensity of putrefactive changes taking place in the intestine. Therefore it occurs in hypochlorhydria (p. 520) from any cause. But in the opposite condition of hyperchlorhydria in gastric ulcer there is also

indicanuria. Indicanuria also occurs in conditions in which there is diminished peristalsis of the small intestine, as in ileus and peritonitis, not in simple constipation; also in conditions in which putrefactive changes occur in the body elsewhere than in the intestine, as in empyema, putrid bronchitis, gangrene of the lungs, etc.

The tests used for the detection and quantitative estimation of indoxyl derivatives in the urine are based upon their decomposition by hydrochloric acid into indoxyl and sulfates, and the oxidation of the former to indigo blue.

*Obermayer's* modification of the *Jaffé* method is probably the best: The urine is mixed with 1/5 its volume of 20% solution of lead acetate and filtered. The filtrate is mixed with an equal volume of fuming hydrochloric acid containing 3:1000 of ferric chlorid, a few drops of chloroform are added, and the mixture strongly shaken 1 to 2 minutes. With normal urine the chloroform remains colorless or almost so; but if an excess of indoxyl compounds be present the chloroform is colored blue, and the depth of the color is a rough indication of the degree of the excess. The best method of more exact quantitative determination is Müller's spectrophotometric method, which is based upon the same principle as Vierordt's method of hæmoglobin determination (p. 556), and requires similar apparatus.

**Skatoxyl-sulfates—Urohæmatin**—correspond in constitution to the indoxyl-sulfates, and have a similar origin. Like the indoxyl compounds, they are chromogens, and on decomposition they yield red or violet coloring-matters, which are referred to as "indigo red." When the Obermayer test as above described, but before addition of chloroform, is applied to urine containing excess of skatoxyl compounds, it becomes red or violet in color, and chloroform when added and shaken with the liquid is colored red or violet. The "reaction of Rosenbach " is due to urohæmatin. It consists of the addition of concentrated nitric acid drop by drop to the boiling urine, which, in presence of excess of the chromogen urohæmatin, assumes a deep wine-red color, which is usually tinged blue from the presence of indigo blue. Such urines also turn darker, reddish, violet, or even black, from the surface downwards, on mere exposure to air.

**Urinary Pigments and Chromogens.**—The yellow color of the urine is due to the presence of more than one coloring-matter. The most abundant of those constantly present is **urochrom**, which is accompanied by small quantities of hæmatoporphyrin (p. 551), and by a chromogen, **urobilinogen**, which, shortly after the urine is voided, gives rise to the coloring-matter, **urobilin**. Besides these and the indoxyl- and skatoxyl-compounds already mentioned, the urine frequently contains a red coloring-matter, **uroerythrin**, which is, however, not constantly present. A number of urinary coloring-

matters have been named, which are probably one of the above-mentioned or products of the action of acids or of other reagents upon them or upon other constituents of the urine.

Urochrom (of Garrod)—is closely related to urobilin, from which it differs in not being precipitated by saturation of its solution with ammonium sulfate, and in not giving either the spectrum or the fluorescence of urobilin. The two substances are readily converted one into the other; urochrom into urobilin by the reducing action of aldehyde, and urobilin into urochrom by moderate oxidation with permanganate. Urochrom contains nitrogen, but no iron; it is amorphous, brown, soluble in water and in dilute alcohol, sparingly soluble in strong alcohol, amylic alcohol or acetic ether, insoluble in ether, chloroform or benzene. It is precipitated by lead acetate, silver nitrate, or mercuric acetate.

Urobilin (of Jaffé)—does not exist in fresh urine, but is formed from urobilinogen, probably by the action of light. There are some differences in the properties of urobilins, as described by different observers, and there may be several urobilins, or urobilinoids, normal, febrile, etc. Urobilin-like substances have also been obtained from bilirubin, from hæmatin and from hæmatoporphyrin, and, as they have been formed both by reduction and by oxidation, they cannot be identical with each other. Urobilin is apparently identical with the stercobilin of the fæces, which is formed in the intestine from the bile-pigments. Both the urinary and the fæcal pigment are increased in amount with increased intestinal putrefaction.

Urobilin is amorphous, reddish-brown to reddish-yellow, soluble in alcohol, amylic alcohol and chloroform, less soluble in ether, sparingly soluble in water, in which its solubility is increased by the presence of neutral salts. It is precipitated completely from its solutions by saturation with ammonium sulfate after addition of sulfuric acid. It is soluble in alkalies, from which solutions it is precipitated by acids. It is precipitated from neutral or faintly alkaline solutions by lead acetate, and by zinc sulfate, but not by mercuric salts. It does not give the Gmelin reaction, but gives a reaction similar to the biuret reaction. Its concentrated, neutral, alcoholic solutions are brown in color; the dilute solutions yellow or rose-colored, and showing a strong green fluorescence. The acid solutions have the same colors, are not fluorescent, but show a faint absorption band between b and F. If zinc chlorid be added to the ammoniacal solution it becomes red, and shows a fine green fluorescence. This solution gives a broad absorption band, extending from about midway between E and b very nearly to F; and, if concentrated, a second band over E appears on careful acidulation with sulfuric acid.

The chromogen, **urobilinogen,** is a colorless substance, which may be obtained by precipitation, caused by saturation of the urine with ammonium sulfate; or may be extracted from the urine, acidulated with acetic acid, by agitation with acetic ether. It is soluble in chloroform, ether and amylic alcohol. Its solutions give no spectrum, and, on exposure to light, soon become colored, from conversion of the urobilinogen into urobilin.

The quantity of urobilin eliminated in 24 hours has been variously estimated as from 30 to 140 mgm. Hoppe-Seyler's method of determination consists in acidulating 100 cc. of urine with $H_2SO_4$, precipitating by saturation with $(NH_4)_2SO_4$, collection of the precipitate after 24 hours, washing with saturated $(NH_4)_2SO_4$ solution, extraction of the residue with a mixture of equal parts of chloroform and alcohol, removal of alcohol by agitation of this, filtered, solution with water, evaporation of the chloroform solution in a weighed beaker, drying at 100°, washing the residue with ether, drying, and weighing. By this method Hoppe-Seyler found a mean of 123 mgm. in 24 hours, and extremes of 80 and 140 mgm. A spectrophotometric method, based upon the same principle as those for hæmoglobin and for indican, also gives good results.

Pathologically the elimination of urobilinogen is increased in conditions involving increased metamorphosis of blood corpuscles, in fevers, and in icterus, in chronic lead poisoning, and in acute poisoning by antipyrin and antifebrin.

**Uroerythrin** exists in small quantity in normal urine, and is the substance which gives a pink or red color to "lateritious deposits." It is soluble in amylic alcohol, forming solutions which are rose-colored if dilute, orange or fiery-red if concentrated, which are not fluorescent, and which give a spectrum of a single band, broader than that of urobilin, extending from midway between D and E nearly to F, with a lighter part between E and b. Its solutions are colored carmine-red by $H_2SO_4$, and grass-green by alkalies. A rough method for detecting its presence in excess consists of precipitating the urine with lead acetate, and allowing the precipitate to settle for 15 minutes in the dark. In presence of excess of uroerythrin the precipitate is distinctly pink, otherwise it is white.

Uroerythrin is increased in amount in the urine after violent exercise, after excess of food or of alcohol, in disturbances of digestion, fevers, and derangements of the hepatic circulation.

**Cystin,** $C_3H_6NSO_2$, which will be further considered under the pathological constituents, is really a normal constituent of the urine, but is present only in traces, not exceeding 0.01 gm. in 24 hours.

**Reducing Substances.**— The reducing power of uric acid has been noticed (p. 355). The normal urine also contains traces of

glucose, not sufficient to react with the ordinary reduction tests, but recognizable by them after concentration and extraction. A near product of oxidation of glucose, glucuronic acid, $CHO.(CHOH)_4.COOH$ (p. 299), is also present in conjugate combination with indoxyl, skatoxyl, and phenolic radicals, and, when they are present, with camphor as campho-glucuronic acid and with chloral as urochloralic acid. Glucuronic acid is formed as an intermediate product in the oxidation of glucose, and only appears in the urine when protected from further oxidation by combination in one of the forms mentioned. The conjugate glucuronic acids are lævogyrous, while the acid itself is dextrogyrous. They are readily hydrolysed by dilute acids, with liberation of glucuronic acid. Thus urochloralic acid is decomposed into glucuronic acid and trichloralcohol: $CCl_3.CO.CH_2.(CHOH)_4.COOH + H_2O = CHO.(CHOH)_4.COOH + CCl_3.CH_2OH$. Glucuronic acid is a syrup, but forms crystalline salts; it is very soluble in water and in alcohol; it reduces the salts of copper, silver and bismuth; is not fermentable, gives the furfurol reaction, also the phloroglucin reaction of the pentoses, and forms a crystalline compound with phenylhydrazin, which fuses at 115°.

**Oxalic Acid**—is a normal constituent of the urine in small amount, not exceeding 0.02 gm. in 24 hours, and is present as calcium oxalate, held in solution by the acid reaction of the monosodic phosphate. It is partly taken in with the food, as it exists in many fruits and vegetables, apples, spinach, sorrel, asparagus, rhubarb, etc. But it is also produced in the system from proteins and fats, as it does not disappear from the urine when the diet is limited to these, or with deprivation of food. Calcium oxalate is frequently deposited from subacid urines either in octahedral crystals or in dumb-bells, and sometimes forms calculi, mulberry calculi, which are white, hard and nodulated. The elimination of oxalic acid is increased in intestinal disturbances, sometimes with transient albuminuria, and sometimes in diabetes. Idiopathic oxaluria, or the oxalic acid diathesis, is a condition in which the elimination of oxalates is notably increased, the cause of which is unknown. In oxalic acid poisoning the elimination of the poison takes place through the kidneys, and the tubules become plugged with crystals of calcium oxalate.

For the quantitative determination of oxalic acid 500 cc. of urine are treated with $CaCl_2$, rendered alkaline with ammonium hydroxid, and then acid with acetic acid. In 24 hours the precipitate is collected upon a small filter, washed with water, and extracted with dilute hydrochloric acid (which leaves the uric acid upon the filter). The acid solution is again alkalized with ammonium hy-

droxid and the precipitate collected upon a small filter, washed, dried, burnt, strongly ignited and weighed as calcium oxid. The weight of CaO found, multiplied by 2.2857, gives the amount of calcium oxalate; or, multiplied by 1.6071, the amount of oxalic acid in 500 cc. urine.

**Other Constituents.**—Besides the above, the urine contains a number of other substances, present in small amount or imperfectly identified.

The total sulfur of the urine is greater in amount than can be accounted for by the mineral and ethereal sulfates, the excess being about 20% of the whole. This is sometimes referred to as "neutral sulfur" in contradistinction to the "acid sulfur" of the sulfates. A small portion exists in cystin (pp. 593, 617), and the remainder in substances of very diverse nature. Among these are: (1) a **thiocyanate**, present to the amount of about .04 to .11 p/m; (2) **taurocarbamic acid**, $NH_2.CO.NH.C_2H_4.SO_2.OH$, and (3) **taurin** itself, derived from the decomposition of taurocholic acid; (4) **oxyproteic acid**, a compound containing nitrogen and sulfur, increased in amount in the urine of dogs poisoned with phosphorus, which does not give the xanthoproteic or biuret reactions, but gives a weak Millon reaction; (5) **chondroitin-sulfuric acid**, an ester-sulfuric acid containing nitrogen, of interest in connection with the occurrence of albumen in the urine (p. 603); and (6) a **nucleoalbumen**, containing sulfur, which constitutes the so-called mucus, or "nubecula."

Nor do the phosphates of the urine account for all of the phosphorus which it contains: an amount corresponding to about 0.05 gm. $P_2O_5$ in 24 hours exists in some form of organic combination, such as phosphoglyceric or phosphosarcic acid.

Human urine, when injected into the circulation of animals, is quite poisonous. Thus rabbits are killed by an average amount of 45 cc. of normal human urine per kilo of weight of the animal, injected at one time. The urine of persons suffering from febrile diseases is more actively poisonous than that of healthy individuals. The urine excreted in the early morning hours is more active than that formed during the day and early night, and the night urine produces convulsions, while the day urine behaves as a narcotic poison. The urine of some of the lower animals, notably that of the cat, is still more poisonous to rabbits than human urine. The toxicity of the urine is referable in part to the action of the potassium salts (p. 182), but it is not proportionate to their quantity. It is estimated that about 45% of the poisonous action is due to potassium compounds; the remainder being due in part to the urinary coloring-matters, in part to the moderately toxic quality of urea, uric acid, etc., and in part to the presence of urinary leucomaïns, so-called

ptomaïns. Several observers have obtained minute quantities of basic, actively poisonous substances, having the general characters of the alkaloids, from normal urine, and in larger amount from febrile urine. The exact chemical nature of these bodies is not determined, although one of them, Pouchet's base, has been obtained in the crystalline form, and was found to have the composition $C_7H_{14}N_4O_2$, or $C_7H_{12}N_4O_2$. True ptomaïns, such as cadaverin, putrescin, and other diamins have also been found in pathological urines, notably in cystinuria.

### ABNORMAL CONSTITUENTS.

Of the following substances some, such as albumin, hæmoglobin, etc., are literally abnormal to the urine, that is their presence in any amount is the result of a pathological condition; others, such as glucose, cystin, etc., are considered abnormal for reasons of convenience; they are normally present, but only in very minute quantities, insufficient to be revealed by the tests customarily used, but are much increased in amount in certain pathological conditions.

**Proteins.**—The proteins which may occur in the urine are serum albumin, serum globulin, albumoses, including Brücke's peptone, and histon, a nucleoalbumen, fibrin, and hæmoglobin.

**Serum Albumin and Serum Globulin** — are usually included in the term "albumin," as clinically applied to the urine, as both respond to the tests generally used. The question whether albumin is or is not a strictly normal constituent of the urine, in the sense above indicated, has been much discussed. The weight of evidence is, however, in favor of the view that the presence of albumin is always an abnormal condition. That it may be present, however, in quantities as large as 25 to 75 mgm. to the litre, in the urine of persons under conditions which are not absolutely pathological, although departing from those which are usual, cannot be denied.

Serum albumin and serum globulin appear in the urine in a great variety of abnormal conditions, usually in quantity not exceeding 5 p/m, rarely reaching 10 p/m, and very exceptionally 50 p/m. (1) *Functional albuminurias* include those conditions which are sometimes considered as so-called "physiologic," or normal albuminurias, in which the presence of albumin is transitory and due to an exaggeration or deficiency of some normal condition; after severe muscular exertion, under great mental strain or emotion, in anæmic children and youths, accompanying excessive elimination of uric or oxalic acid, alimentary albuminuria due to excess of protein diet, particularly if raw. (2) *Febrile*, in most acute febrile diseases, particularly during convalescence. In typhoid it is always present, and disap-

pears on the fifth to the eighth day in light cases, on the tenth day or later in severe cases. In pneumonia albumin is always present, sometimes abundantly. In any acute febrile disease albumin may be present, without the existence of any structural change in the kidney. (3) *Circulatory*, due to disturbances of the blood-pressure, in which the quantity of albumin is usually small, as in valvular heart-lesions, degeneration of the heart muscle, diseases of the coronary arteries, impeded pulmonary circulation, in pregnancy by pressure upon the renal veins, after cold baths, in intestinal catarrh and in Asiatic cholera. (4) *Hæmic*, due to pathologic modification of the blood proteins, in purpura, scurvy, leukæmia, pernicious anæmia, jaundice, diabetes, and syphilis. (5) *Toxic*, by the action of hæmatic poisons such as lead, mercury, chloroform, or by irritating action upon the glandular epithelium of the kidney, such as is caused by mercury, cantharides, oxalic acid, mineral acids, iodin, phosphorus, arsenic, antimony, carbolic acid, salicylic acid, turpentine, and nitrates. (6) *Accidental*, by the presence in the urine of blood, pus, or semen. So far as the two former are concerned, they may be either renal, or post-renal in origin. (7) *Nephritic*, in acute nephritis albumin is present in large amount, as much as 5 to 20 gm. in 24 hours, and the sediment contains casts. In chronic parenchymatous nephritis albumin is also constantly present, and in still larger quantity, as high as 15 to 30 gm. in 24 hours. In chronic interstitial nephritis the amount is small, rarely exceeding 2 to 5 gm. in 24 hours, and variable, while casts may be absent. In amyloid degeneration the amount is usually small, although it may reach 10 gm. in 24 hours. In this condition the proportion of serum globulin to serum albumin is greater than in other kidney lesions, it is usually from 1:0.8 to 1:1.4. Pure globinuria, that is the presence in the urine of serum globulin, unaccompanied by serum albumin, has not been observed.

For the **detection of serum albumin and serum globulin** in the urine it must be perfectly clear. If not so it is to be filtered, and if this does not render it transparent, it is to be treated with a few drops of magnesia mixture (p. 121 note), and again filtered. Or the urine is shaken with kieselguhr (diatomaceous earth) and filtered.

(1) *Heat and nitric acid test.*—The clear urine, if alkaline, is rendered *just* acid by addition, guttatim, of dilute acetic acid (nitric acid should not be used, and the acidulation is imperative). The urine is now heated to near boiling, and if a cloudiness or coagulum be formed, nitric acid is added slowly to the extent of about ten drops. If heat produces a cloudiness which clears up completely on addition of nitric acid, it is due to excess of earthy phosphates. If a cloudiness caused by heat do not clear up (it may increase) on addition of nitric acid, it is due to serum albumin or serum globulin.

Sometimes the urine after heating and addition of nitric acid deposits a granular sediment on cooling; this is due to the separation of urates.

(2) *Heller's test*—is more delicate than the above, and reacts with urine containing 0.002 per cent. of albumin. About 1 cm. of nitric acid is placed in a test-tube, which is then held at an angle and the urine is allowed to flow slowly from a pipette upon the surface of the acid (Fig. 40) so as to form a distinct layer with the minimum of mixing of the two liquids. The procedure frequently directed, of "underrunning" the acid from a pipette under the urine, placed in a test-tube, does not give as good results. After withdrawing the pipette, the test-tube is returned to the vertical slowly, and the line of junction of the two liquids examined against a dark background. If the urine contain albumin a white, opaque band, whose upper and lower borders are *sharply defined*, will be seen at the line of junction of the two liquids. *A colored band* is generally observed in applying this test, which has no relation to the presence of albumin, it may be of some shade of red from the presence of excess of normal coloring matter, or, of uroerythrin, blue, or almost black, from the presence of indican in excess, or giving the colors of the Gmelin reaction (p. 528) in the presence of bile. When urates are present in excess a white zone is also formed which, however, differs from that caused by coagulation of albumin in the following particulars: it is not at, but slightly above, the line of contact of the two liquids; while its lower border may be sharply defined, it has no upper border, but shades off gradually in the upper layer; and it is not produced with the urine diluted with one or two volumes of water. When urea is present in excess, crystals of urea nitrate separate (p. 582), but these differ widely in appearance from the amorphous coagulum of albumin; are formed throughout the liquid after a short time; and are not produced with the diluted urine. Occasionally the urine contains resinous substances, usually administered as medicines, which with Heller's test give a zone resembling that produced by albumin. This may be distinguished by removing the portion of the liquid containing the ring by means of a pipette and shaking it in another test-tube with a little ether, when it will clear if it be resinous, but will remain cloudy if albuminous. Sometimes undiluted urines give no immediate reaction, and only a faint, ill-defined ring after standing,

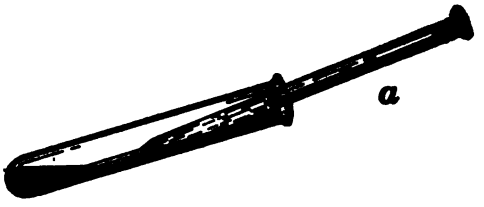



FIG. 40.

but the diluted urine gives an immediate and well-defined reaction; this is caused by the so-called nucleoalbumen (p. 603). True mucin may also produce a faint opalescence, but no well-defined ring, and the opalescence disappears on slight rotation of the tube. The primary albumoses respond to the Heller test, but they redissolve on heating the test-tube, and they are not coagulated by heat, hence the heat test should always be used as well as the Heller.

(3) *Precipitation by Neutral Salts.*—Several tests are in use, based upon the precipitation of albumin from acid solutions by saturated solutions of neutral salts, such as sodium sulfate, magnesium sulfate or sodium chlorid. *Roberts' reagent* consists of a saturated solution of sodium chlorid containing 5 per cent. of strong hydrochloric acid, and filtered if necessary. The urine is floated upon the warmed reagent in the same manner as in the application of Heller's method; and a milky zone indicates the presence of albumin. Albumoses are also precipitated, but not urates; nor does the colored zone appear.

If acetic acid be added to albuminous urine to strongly acid reaction, and then an equal volume of saturated sodium sulfate solution, and the mixture boiled, the albumin is completely precipitated, while the albumoses remain in solution in the hot liquid. This reaction, designated as Panum's method, is utilized to free the urine from albumen in testing for albumoses (p. 602).

*Other Precipitation Tests.*— Several of the precipitation reactions of the albumens (p. 502) have been utilized for the detection of albumen in the urine. Prominent among these are the following:

(4) *Ferrocyanid Reaction.*—Acetic acid is added to the urine in such amount as to be present in the proportion of 2%, and then a 1:20 solution of potassium ferrocyanid drop by drop. A cloudiness or flaky precipitate is produced by serum albumin, serum globulin, or primary albumoses, but the last named are redissolved by addition of much acetic acid and warming. The test is quite as delicate as the Heller. If the addition of acetic acid alone produce a cloudiness, it is due to the presence of mucin or of mucin-like substances, and the urine is to be filtered before addition of the ferrocyanid.

In the following tests the urine is to be floated upon the surface of the reagent in the same manner as in the application of the Heller test, and the characteristic appearance is also the formation of a milky zone.

(5) *Trichloracetic Acid Reaction.*—This reaction is still more delicate than the Heller. A strong solution of the acid (sp. gr.= 1.14) is used, or a crystal of the acid is dropped into the urine, and, dissolving, it forms a layer at the bottom. Serum albumin, serum globulin and primary albumoses respond to the test, but the

redissolve on heating, while the others remain. Excess s also gives rise to the same appearance as with the Heller n, and, similarly, its formation is prevented by previous dilu- the urine. The colored zone produced by urinary pigments in ller test is not formed with this or with the following reagents.

(6) *Spiegler's Reagent* — consists of 8 gms. of mercuric chlorid, ms. of tartaric acid and 20 cc. of glycerol, dissolved in 200 cc. of er. A few drops of acetic acid are to be added to the urine for test, which is said to be the most delicate of those for albumin. limit is placed at 1:250.000, and it is frequently observed with mal urine. The sp. gr. of urines below 1.005 is to be raised ldition of salt solution before application of the test. Primary noses give the reaction, dary albumoses (urinary pep- do not.

(7) *Tanret's Reagent* — dissolving 1.35 gm. of mer- c chlorid and 3.32 g ssium iodid in separate por- s of water, mixing the naking the bulk up to 60 cc., nd adding 20 cc. of glac id. Secondary albumoses are precipitated, but rediss ating. Certain alkaloids are also precipitated, but they a ed by ether shaken with the aqueous liquid, which then be near. Several other reagents, containing mercuric salts (Bo at's, Jolle's, Zouchlos', Für- gringer's) are in use.

(8) *Oliver's Reagent* is one of several (Sonnenschein's, Maschke's, Jaowrowski's) containing tungstates or molybdates. It is a mixture of equal parts of a 20% solution of sodium tungstate, and 60% solution of citric acid. It precipitates secondary albumoses, which, however, dissolve on heating, and also alkaloids.

(9) *Roch's Reagent*, Salicylsulfonic acid, and (10) *Riegler's Reagent*, β-naphthol-o-sulfonic acid (asaprol), and orthophenol-sulfonic acid (aseptol), are used in the same manner as trichloracetic acid. They precipitate albumoses, which redissolve on heating.

(11) *Esbach's Reagent* — is one of several containing picric acid. It contains 10 gms. of picric acid and 20 gms. of citric acid in the liter. It is mixed with or floated upon the urine. It precipitates all proteins, also uric acid, creatinin and certain alkaloids.

(12) *Metaphosphoric Acid* — is best used in the form of *Blum's reagent*, which consists of a 10% solution of the acid, to which have been added 0.05 gm. of manganous chlorid, dissolved in a little dilute hydrochloric acid, and a little lead peroxid, and the solution filtered. The reagent should not be used if it have lost its pink color. It precipitates albumoses and uric acid.

The color reactions of the albumens (p. 502) cannot be applied to the urine.

**Test for Globulin.**—Neutralize the urine exactly with ammonia, filter, and add an equal volume of neutral, saturated solution of ammonium sulfate: globulin separates as a white, flocculent precipitate. Albumin may be tested for in the filtrate from this precipitate by acidulation with acetic acid and heating. Excess of urates may give rise to a precipitate in using this test, but it is only formed after a time, is not flocculent, but granular, and is not white, but colored.

**Quantitative Determination of Albumin and Globulin.**—The only method of determining the quantity of "albumin" with any degree of accuracy is gravimetric. From 20 to 100 cc. of the clear urine (according as the qualitative testing has indicated a large or a small quantity of albumin) are made up to 100 cc. of liquid by addition of water, if necessary, and slowly heated. As the boiling temperature is approached, 2–4 drops of dilute acetic acid are added, and the mixture boiled for a few minutes, until the coagulated albumin has become flocculent, when it is collected upon a weighed filter, washed, first with water containing a little nitric acid, then with boiling water, then with alcohol, and finally once or twice with ether, dried at 110°, and weighed. For accurate determinations, the filter and coagulum are burnt and moderately ignited, the ash weighed, and its weight subtracted from that of the albumen found.

**Quantitative Determination of Globulin.**—One hundred cc. of the clear urine are accurately neutralized with ammonia, an equal volume of a neutral, saturated solution of ammonium sulfate is added and the mixture allowed to stand for an hour, after which the precipitated globulin is collected upon a weighed filter, washed with one-half saturated ammonium sulfate solution, dried at 110°, extracted with boiling water, then with alcohol, and then with ether, dried again at 110°, and weighed. The filter and contents are then burnt, ignited, cooled and weighed, and the weight of the ash subtracted from the weight of globulin, plus ash, previously obtained. To determine the relation between albumin and globulin a determination of albumin and globulin, and another of globulin alone are made, as above directed; the difference is the amount of albumin.

**Albumoses (Peptones).**—Substances similar to the products of the action of digestive enzymes upon proteins occur in the urine pathologically. Peptones in the modern sense, i. e., not precipitable by saturation with ammonium sulfate, do not appear in the urine normally or pathologically. In the condition designated as "peptonuria," the so-called "urinary peptone" consists principally of substances closely resembling, if not identical with, the secondary albumoses, (deutero-albumoses, p. 518). Peptonuria in this sense occurs in a variety of pathological conditions: in diseases attended with the

formation of large deposits of pus, in yellow atrophy and in abscess of the liver, in certain intestinal diseases, including typhoid, in tubercular ulceration, in scurvy, pyæmia, septicæmia, leukæmia, in diseases of pregnancy, in endocarditis, in pneumonia, in pleurisy, in diphtheria, in suppurative meningitis, and in certain forms of poisoning.

Primary albumoses, hetero-albumoses, have been met with in the urine (albumosuria) only exceptionally in a few cases of osteomalachia.

The presence of albumoses is best detected by Panum's method (p. 599): acetic acid is added to strongly acid reaction and then an equal volume of saturated sodium sulfate solution, and the liquid is heated to boiling and filtered hot; albumoses are precipitated before the boiling, are redissolved on boiling, and are again precipitated from the filtrate on cooling.

If nitric acid be added to the hot filtrate from the coagulated albumin, produced by boiling a urine containing albumin and albumoses, no immediate precipitation occurs, but on cooling a white or yellow precipitate of albumose separates, which redissolves on heating, and reappears on cooling.

Heteroalbumose (primary albumose) gives the above reactions, and is further characterized by its action with the heat test: at a temperature of about 60° the urine becomes milky and deposits an imperfectly flocculent, gummy material, which adheres to the walls of the beaker, and which, in an acid liquid, dissolves on boiling, to reappear on cooling again.

For the detection of small quantities of secondary albumoses (urinary peptone) the method of Hofmeister, although intricate, is the most reliable. It consists in the complete removal of albumin by precipitation with ferric chlorid, the precipitation of the albumose with phosphotungstic acid, the decomposition of the precipitate, and the application of the biuret reaction to the solution of albumose. The student is referred to more comprehensive treatises for the details of the process.

**Mucin-like Substances.** — The urine sometimes contains true mucins and nucleoproteids, produced in the urinary tract below the kidneys. The "nubecula" (p. 566) which separates as a delicate cloud from normal urine on standing, has for its chief protein constituent a substance resembling ovimucoid (p. 504), and designated as urinary mucoid. It is a glycoproteid, which on heating with dilute acids, yields a reducing substance, but no sulfuric acid (see p. 603). It is soluble in dilute alkaline solutions, from which it is precipitated by acetic acid, but soluble in an excess of the acid. It is similarly precipitated by, and soluble in excess of mineral acids.

It is not coagulated by heat, even in presence of sodium chlorid to saturation; but it is precipitated in the cold by saturation with magnesium or ammonium sulfate.

The substance usually referred to as nucleoalbumen, or as mucus, in the urine consists of different protein-coagulating substances, among which are nucleic acids, taurocholic acid, especially in icterus, and particularly

**Chondroitin-sulfuric acid,** which is present in small amount in normal urine, and is increased in diseases involving the renal and vesical epithelium, as in acute and chronic nephritis and in cystitis, also in "functional" albuminuria, in icterus, and from the action of many poisons, notably of corrosive sublimate, arsenic, pyrogallic acid, naphthol and anilin. This substance exists in the urine, as well as in cartilage, in combination with albumens in the form of chondroproteids, or chondroalbumens, the first products of decomposition of which are a protein and chondroitin-sulfuric acid. The latter is an amorphous substance, easily soluble in water, strongly acid in reaction, precipitable from its solution by alcohol in presence of excess of salts, or by a large amount of glacial acetic acid, not precipitated by dilute acetic acid, mineral acids, picric acid or tannin. With albumin it forms a precipitate, soluble in acids and in alkalies. It is an ester-sulfuric acid (p. 589), having the composition, $C_{18}H_{26}NO_{13}SO_3OH$, which on heating with dilute acids, is decomposed into sulfuric acid and **chondroitin,** $C_{18}H_{27}NO_{14}$, which is a monobasic acid, itself decomposed by further heating with dilute nitric acid into acetic acid and **chondrosin,** $C_{12}H_{21}NO_{11}$, the latter an amido-acid which reduces alkaline solutions of copper salts on heating.

The chondroproteids react with the Heller test, and their presence in excess is to be suspected when the urine becomes cloudy on addition of acetic acid in the cold, and gives a more distinct Heller reaction after dilution than when undiluted. To separate and identify chondroproteids a large volume of urine is treated with chloroform to prevent decomposition, and submitted to dialysis to remove salts; acetic acid is then added in the proportion of 2 p/m, and the mixture allowed to stand until the precipitate settles. This is then dissolved in the smallest quantity of dilute alkali and again precipitated with acetic acid. The precipitate is then heated on the water-bath with 5 per cent. hydrochloric acid and the solution divided into two parts, one of which is tested for its reducing action by Fehling's solution, and the other for sulfuric acid by barium chlorid.

A histon, a phosphorized protein, apparently identical with nucleo-histon, has been met with in the urine in a case of leukæmia, and also in cases of peritonitis following appendicitis, pneumonia, erysipelas and scarlatina.

**Hæmoglobin.—The blood coloring-matter may exist in the urine in the two conditions of hæmaturia and of hæmoglobinuria. The former is the consequence of a hæmorrhage somewhere in the urinary tract, the latter of profound alteration in the blood, and elimination of the liberated hæmoglobin. In the former condition the sediment contains blood-corpuscles, and sometimes blood-casts or small clots, and albumin is present in the urine, whose color is bright-red, reddish-brown, or dark-brown. The location of the hæmorrhage cannot be determined by examination of the urine, although it may be noticed that, if it is urethral, the last portions of the urine passed are free from blood; if it is renal, blood-casts are usually found in the sediment, and, if it is vesical, blood-clots of considerable size may be present.**

**Hæmoglobinuria, in which the urine contains oxyhæmoglobin or methæmoglobin in solution, with no blood-corpuscles, or very few, in the sediment, is most frequently the result of poisoning, as by hydrogen arsenid, potassium chlorate, pyrogallol and naphthol, but it also occurs in malarial fevers in the tropics, and after severe burns or after transfusion of blood. The urine varies in color from bright-red to dark-brown.**

***Tests for Blood-pigment.*—(1) The urine, suitably diluted if necessary, gives the spectrum of oxyhæmoglobin, or that of methæmoglobin (p. 547). (2) *Heller's test:* the faintly acid urine is boiled, when a dirty brownish coagulum of albumin, containing the blood-pigment, is formed. Sodium hydroxid is added to the hot liquid, which then clears, becomes greenish in thin layers, and on standing deposits a red material having greenish reflections, which consists of phosphates and hæmatin. This precipitate may be collected and used for (3) *Teichmann's test* (p. 550). (4) *The guaiac reaction:* the urine is rendered faintly acid if not already so, and upon its surface is floated a mixture of equal parts of tincture of guaiac and old oil of turpentine. In the presence of blood coloring-matter a white zone is produced, which soon turns bluish, greenish, and finally a brilliant blue, and on gently shaking the tube the whole liquid is colored blue if the quantity of pigment is sufficient. In the reagent ozonic ether (ether containing hydrogen peroxid) may be used in place of oil of turpentine. Pus gives a similar color with tincture of guaiac alone.**

**Hæmatoporphyrin, related to urobilin and isomeric with bilirubin, is a normal constituent of the urine in small amount, but is notably increased in amount in poisoning by sulfonal, trional and tetronal, or even after long-continued medicinal administration of these remedies; also, in hepatic cirrhosis and in croupous pneumonia. Usually it colors the urine red, sometimes of a dark port-wine color,**

but it may be present in considerable amount in urines which it colors only slightly. It is not accompanied by albumin.

To test the urine for hæmatoporphyrin 100 to 200 cc. are precipitated with 10% sodium hydroxid solution; the precipitate, of phosphates and coloring-matter, is dissolved in about 10 cc. of alcohol acidulated with hydrochloric acid, and the solution is examined with the spectroscope (p. 551). If the result be negative the alcoholic solution is rendered alkaline with ammonium hydroxid, the precipitate dissolved in a little dilute acetic acid, agitated with chloroform, and the chloroform solution again examined spectroscopically.

**Biliary Constituents.**— The urine may contain the biliary salts and pigments as a consequence of reabsorption of bile, caused by obstruction of the biliary ducts, or when the blood-pressure in the liver is lowered (hepatogenic icterus); or the biliary pigments may appear in the urine in consequence of their formation in the system elsewhere than in the liver, as hæmatoidin is produced from the blood coloring-matter (p. 528), as in pernicious anæmia, malaria, typhoid, and in poisoning by hydrogen arsenid (hæmatogenic icterus). Urine containing bile is golden-yellow or greenish-brown in color, and the epithelium which it contains is also dyed yellow. It is usually cloudy, contains albumin, and, when shaken, forms a yellow, persistent froth upon its surface.

The biliary salts are rarely tested for, because the examination for the equally characteristic coloring-matters is much more easily conducted. They may, however, be detected by the Pettenkofer reaction, if care be had to avoid possible sources of error from other substances which also respond to the test. To this end the urine is concentrated, extracted with alcohol, and the alcoholic extract filtered and freed from alcohol by evaporation. The residue is dissolved in a little water and precipitated with lead acetate and ammonia. The lead precipitate is collected, washed, extracted with boiling alcohol, which is filtered off hot, treated with a little sodium hydroxid solution and evaporated to dryness. The residue is extracted with a little absolute alcohol, the solution mixed with about ten volumes of perfectly anhydrous ether, the precipitate collected on a small filter, washed with a little ether, dissolved in a small quantity of water and tested by the Pettenkofer method as directed on p. 527.

For the detection of the biliary coloring-matters the reactions described on p. 528 are used. The Gmelin reaction may be modified to Rosenbach's method, which consists in filtering the urine through a small filter, and touching the dried filter with a drop of nitroso-nitric acid, when the colors are produced in rings about the drop. This reaction is not satisfactory in dark urines containing excess of indican. In using Hammarsten's reaction with urines containing

blood coloring-matter, or very small quantities of bile pigments, a preparatory treatment is required, which consists in adding barium chlorid to the urine, centrifugating, pouring off the supernatant liquid, shaking the sediment with 2 cc. of the reagent, and centrifugating again, when a bluish-green solution is obtained. Smith's reaction may also be used: float dilute tincture of iodin (1:10) on the urine, when the biliary pigments form a green ring at the union of the two layers.

**Other Abnormal Pigments**—*Urorosein* is a coloring-matter, not present in normal urine, but appearing in a variety of abnormal conditions, as in diabetes mellitus, chlorosis, osteomalachia, nephritis, typhoid fever, phthisis, pernicious anæmia, etc. It exists in the urine as a chromogen, from which it is formed by the action of acids, and, when so liberated, communicates a rose-color to the urine. It produces the rose-colored ring so frequently observed in applying the Heller test to the pathological urines. To demonstrate its presence 10 cc. of 1:4 sulfuric acid are added to 50 cc. of urine, which are then shaken with a few cc. of amylic alcohol, and the amylic alcohol examined spectroscopically. Urorosein gives a spectrum of one band between D and E, and in concentrated solution, allows only the red and orange rays to pass. The color is discharged by alkalies, and returns on addition of acids, it is also discharged by agitation of its acid solution with powdered zinc, and reappears soon by exposure to air.

*Melanin* is formed from melanogen on exposure to air of the urine of patients with melanotic tumors. Such urines are normal in color when first voided, but become dark or even black on standing. They may be distinguished from urines behaving similarly from the presence of derivatives of carbolic acid, salol, etc., by the facts that they give with bromin-water precipitates which, although at first yellow, gradually change to black, and that with ferric chlorid they give precipitates which are at first gray, changing to black.

*Alkaptonuria* is another rare condition in which the urine, normally colored at first, turns dark on standing, and which occurs in individuals suffering from tuberculosis or from cerebral tumors. It is due to the presence of aromatic oxyacids, notably of glycosuric acid (pp. 405, 406) which on decomposition yield colored phenolic derivatives, probably similar to those which color the urine in poisoning by phenols and diphenols. Glycosuric acid is also of interest in connection with the testing of urine for sugar in dark-colored urines, because it reduces the cupric salts (Fehling's test, etc.), although it does not reduce those of bismuth (Boettger's test), and it does not ferment.

**Ehrlich's Diazo-reaction.**—The urine in typhoid fever contains a

substance which gives a more or less intense red color with diazobenzene-sulfonic acid and ammonia. The reaction, which can be obtained with typhoid urine usually on the fifth or sixth day, but not later than the twenty-second, was at first said to be pathognomonic of that disease, but it is also obtained with the urine of acute pulmonary phthisis, in which, however, it does not appear before the third week and continues to the end, and also in scarlatina, measles, smallpox and other acute febrile diseases. The reagent used is most conveniently kept in two solutions: (1) a saturated solution of sulfanilic acid in a mixture of 50 cc. of hydrochloric acid and 950 cc. of water; and (2) a 0.5 per cent. solution of sodium nitrite. When used 1 cc. of (2) is added to 40 cc. of (1) and the mixture shaken. Equal volumes of the urine and the reagent are shaken together in a test-tube and 1–2 cc. of ammonia are floated upon the surface of the mixture, when, in an affirmative result, a red band is formed at the junction of the liquids. Or a better method of applying the test consists of adding 50 cc. of absolute alcohol to 10 cc. of urine, filtering, adding 20 cc. of the reagent gradually from a burette to 30 cc. of the filtrate in an Erlenmeyer flask, with agitation after each addition, and then slowly adding ammonia, when a red color is produced, which remains permanent when the ammonia has been added in excess. Urines containing biliary pigments become very dark and cloudy.

**Glucose** — is a normal constituent of the urine in small amount, and it is only when the quantity is increased to such a proportion that the sugar is detectable in the unconcentrated urine by the usual tests that "glycosuria" is said to exist. Normally the carbohydrates taken with the food and assimilated are oxidized in the system, and their carbon and hydrogen are finally eliminated as carbon dioxid and water, except for the traces of sugar normally eliminated as such. But there must be a limit to the amount of carbohydrate material which can be utilized by the economy in a given time. This limit appears to vary in different individuals, but may be placed at an amount of carbohydrate equivalent to 100 to 200 gms. of glucose in 24 hours, and probably when glycosuria exists with a daily ingestion of 100 gms. or less of glucose-equivalent it is due to a pathological condition.

*Non-pathological glycosuria* may be observed: (1) with a diet containing more than 200 gms. of glucose-equivalent in twenty-four hours. A pathological alimentary glycosuria occurs with less than 100 gms. glucose-equivalent in hepatic and pancreatic disease and in certain cerebral diseases; (2) in pregnancy and during lactation there is apparently a diminution in the power to utilize carbohydrate material, and glycosuria frequently exists with a diet containing less

than 100 gms. of glucose-equivalent in 24 hours, the daily elimination sometimes rising as high as 30 gms., but being more usually less than 3 gms. It appears towards the end of gestation, and does not disappear entirely until the suppression of the lacteal secretion; (3) in nursing children from about the eighth day to ten weeks; (4) in old persons (70 to 80 years); (5) in extremely stout persons, particularly in females at the menopause, the elimination sometimes reaching 8 to 12 gms. in 24 hours.

*Pathological glycosurias* may be divided into "transitory," in which the quantity of sugar is not large, and its presence not constant; and "permanent," in which sugar is constantly present and frequently in very large amount. *Transitory glycosuria* occurs in certain hepatic derangements, congestion, cirrhosis and amyloid degeneration; in many diseases of the central nervous system, with tumors or hæmorrhages at the base of the brain, in meningitis, concussion, fracture of cervical vertebræ, railway injuries, in epileptic and apoplectic seizures, and also in certain diseases of the peripheral nervous system, as in sciatica and in tetanus; in acute febrile diseases, pneumonia, typhoid, acute articular rheumatism, scarlatina, etc., particularly during convalescence, when the elimination may reach 5 to 50 gms. in 24 hours; under the influence of many poisons, such as curare, chloral, carbon monoxid, morphin, arsenic, and the anæsthetics.

*Persistent pathological glycosuria* is observed principally in two conditions: (1) In lesions of the brain involving the floor of the fourth ventricle; (2) in diabetes mellitus. In this latter condition the sugar may temporarily disappear from the urine, particularly in the earlier stages of the disease, in the early morning urine, and upon regulation of the diet by exclusion of carbohydrates. There is a diurnal variation in the elimination of sugar, the amount passed being less during the night than during the day, the maximum being reached about four hours after the principal meal, and the minimum six or seven hours thereafter. There is great polyuria, the quantity of urine in 24 hours reaching as high as 50 liters. The quantity of sugar varies greatly; an elimination of 200 gms. in 24 hours is by no means uncommon, but, even with this large amount, the elimination may cease entirely, particularly in the morning urine, by exclusion of carbohydrates from the diet, under the influence of intercurrent diseases, or in the later stages, upon the appearance of diabetic coma. Instances have occasionally been reported in which the elimination has reached 400 to 600 gms. in 24 hours, and one instance in which 1376 gms. were discharged in one day. In other severe cases, terminating fatally, the quantity of sugar eliminated has not been large at any time, not exceeding 10 gms. in 24 hours.

The non-disappearance of the sugar from the urine on exclusion of carbohydrates from the diet is usually considered as indicating a more serious condition, even if the quantity be small, than the elimination of a large amount which ceases under those circumstances. The specific gravity of diabetic urine is usually high, 1030 to 1060, but it may be as low as 1012. In true diabetes there is not only glycosuria, but also azoturia, and the increase in the elimination of nitrogen appears to offer a better measure of the intensity of the disturbance than variations in the amount of sugar. In the later stages acetone, fatty acids and fats also appear in the urine (see below).

As has been already indicated (p. 559), glycosurias other than those due to nervous lesions may have their origin in an inability of the liver to transform the carbohydrates into glycogen, or to inability of the muscles to utilize the carbohydrate material, or to diseases of the pancreas.

**Tests for Glucose.**—If the urine be albuminous, it is indispensable that the albumin be separated before any of the tests for sugar are applied. This is done by heating the urine gradually to boiling, with addition of very dilute acetic acid as the boiling temperature is approached, and heating until the albumin has separated in flocks, and filtering. The most commonly used of the tests for glucose depend upon its reducing power, and the existence of other reducing substances possibly present in the urine, referred to above, must be held in mind. In doubtful cases the phenyl-hydrazin and fermentation tests, which are not based upon the reducing action of glucose, should be resorted to.

(1) *Moore's Test*—is more delicate with colorless solutions of glucose than with the urine. Two samples of the urine are taken in two test-tubes of equal size; to one sufficient KHO solution is added to make it strongly alkaline, and to the other an equal volume of water. The alkaline urine is then heated, when, in the presence of sugar, it becomes more deeply yellow or brown in color, and, on addition of $HNO_3$, gives off a molasses-like odor. The second tube is used for comparison.

(2) *Trommer's Test.*—To the urine, in a test-tube, add one-eighth its bulk of KHO or NaHO solution, and then 5% solution of $CuSO_4$ in slight excess, until the pale-blue precipitate, which is at first redissolved, remains permanent. The liquid is then heated just to boiling, but not boiled, when a yellow or orange-colored precipitate of cuprous hydroxid or oxid is formed if sugar be present. Although very generally used by clinicians, and giving good results when the quantity of sugar present is notable but not very large, this test is open to several objections: if the quantity of

sugar be large and a little copper solution be added, the liquid will become yellow without depositing any precipitate, the cuprous oxid formed being held in solution by the excess of glucose. If too much copper salt be added the precipitate may be black or brown (cupric oxid) in place of yellow or reddish. If the quantity of sugar be very small there is no reduction, except upon prolonged boiling, when reduction is also caused by uric acid, creatinin, etc. Reduction is also caused by diphenols, milk sugar, benzoic acid, salicylic acid, glycerol, chloral, sulfonal, and biliary pigments. Limit—0.0025%.

(3) *Fehling's Test.*—A good formula for this reagent, which is also used for quantitative determinations, is: Soln. I, cupric sulfate 51.98 gms., water 500 cc. Soln. II, Rochelle salt 259.9 gms. dissolved in 1000 cc. of a solution of caustic soda of sp. gr. 1.12. When required for use 1 volume of Soln. I is mixed with 2 volumes of Soln. II; 2 cc. of the mixture are heated in a test-tube just to boiling and then transferred to another test-tube. If any reddish precipitate be found adherent to the first tube the solution has deteriorated and should not be used. This is to be expected when the two solutions have not been mixed shortly before using. The urine is now gradually added to the solution, which is raised to the boiling point after each addition. The presence of sugar is indicated by the formation of a reddish precipitate, which forms more or less rapidly according to the proportion present; the result is considered as negative when a volume of urine equal to that of the solution used has been added without the formation of such precipitate. Fehling's test is not open to the first two objections to Trommer's test mentioned above, but it reacts with the substances there referred to. Limit—0.0008%.

(4) *Boettger's Test*—is also a reduction test, and may be applied either in the manner originally indicated or in Nylander's or Almén's modifications. Equal portions of urine are placed in two test-tubes, to each of which enough solution of sodium carbonate is added to make the reaction distinctly alkaline, and to one a little powdered bismuth subnitrate and to the other a little powdered litharge are added. The contents of the two tubes are then heated to boiling, when, if the bismuth powder becomes black and the litharge remains unchanged the presence of sugar is inferred. The purpose of the litharge is to guard against error from the presence of sulfur compounds, which blacken both the bismuth and lead powders. Nylander's solution is made by adding 4 gms. of Rochelle salt, 2 gms. of bismuth subnitrate and 10 gms. of caustic soda to 90 cc. of water, boiling, cooling and filtering. The solution is to be kept in bottles of amber glass. To use the test 1 cc. of the solution is added to 10 cc. of the urine and the mixture boiled, when sugar causes the

formation of a gray or black precipitate. A parallel testing with litharge is also required. An affirmative result is obtained in the absence of sugar after large doses of quinin, but uric acid and creatinin do not react. Limit—0.025%.

(5) *Fermentation Test.*—Three Smith's fermentation-tubes are used, one (A) completely filled with water, one (B) with a dilute solution of glucose, and the third (C) with the urine to be tested, and each containing a little compressed yeast. The three tubes are put in warm place and left over-night, when if gas have collected in B and C and none in A the urine contains sugar; if gas have collected in B, but none in A or C it is absent; under any other circumstances the yeast is at fault. The only substances other than glucose which respond to this test are the other fermentable carbohydrates, lactose, maltose and fructose.

(6) *Phenylhydrazin Test*—depends upon the formation of the crystalline glucosazone (p. 430). To 5 cc. of the urine in a test-tube add as much phenylhydrazin hydrochlorid as can be taken on the point of the large blade of a pen-knife, and about 1½ times that bulk of sodium acetate, and cause the powders to dissolve by warming and, if necessary, the addition of water, and leave the test-tube in a boiling water-bath for one hour, after which cool it by immersion in a beaker of cold water. If glucose be present a deposit of yellow needles will be formed, which, if the quantity of sugar be small, are best detected by allowing the deposit to settle in a pointed tube and examining it with the microscope. The formation of crystalline plates, or of brown, nodular masses does not indicate the presence of glucose. Needle-shaped crystals are also formed by maltose and by glucuronic acid, but they differ from those produced by glucose in their fusing points: glucose =205°, maltose =190°, glucuronic acid =115°. To determine the fusing points the precipitate is collected, dissolved in hot alcohol, the solution filtered, and evaporated, the crystals dried over $H_2SO_4$, placed in a small closed tube attached to the bulb of a thermometer by a pasted slip of paper, and heated in a paraffin bath, the temperature being noted when the material fuses.

(7) *Polarization Test.*—Preparatory to polariscopic examination the liquid must be rendered transparent and colorless, or nearly so. This is accomplished in the case of the urine and other organic liquids by isolation of the sugar, by precipitation either by basic lead acetate, or by benzoyl chlorid, liberation of the sugar and resolution in water. Either operation is rather intricate, and the student is referred to more comprehensive treatises for their description. The decolorized solution is examined with the polarimeter (p. 24), and if glucose be present it will rotate to the right. Maltose also rotates to the right. Oxybutyric acid (p. 615) rotates to the left, and if it be

present in notable quantity, may neutralize or dominate the right-handed rotation of the glucose. But such urines show a greater left-handed polarization after fermentation than before.

For clinical purposes the Fehling or Boettger tests are to be recommended, supplemented by the fermentation or phenylhydrazin test in cases of doubt.

**Quantitative Determination of Glucose.**—(1) ***By the polarimeter.*** —Clear, decolorized urine (see above) is observed by the polarimeter (p. 24) and the mean of half a dozen readings taken as the angle of deviation. From this the percentage of sugar is determined by the formula $p=\frac{a}{52.6\times l}$, in which $p$ = the weight, in grams, of glucose in 1 cc. of urine; $a$ = the angle of deviation; $l$ = the length of the tube in decimeters. The same formula may be used for other substances by substituting for 52.6 the value of $[a]_D$ for that substance. Or a saccharrimeter, which is a polarimeter graduated to read the percentage of glucose directly, may be used. If the urine contain albumen, it must be removed before determining the value of $a$.

(2) ***By specific gravity; Robert's method.***—The sp. gr. of the urine is carefully determined at 25° (77° F.); yeast is then added, and the mixture kept at 25° (77° F.) until fermentation is complete; the sp. gr. is again observed, and will be found to be lower than before. Each degree of diminution represents 0.2196 gram of sugar in 100 cc. of urine.

(3) ***By Fehling's solution.***—The copper contained in 20 cc. of Fehling's solution (p. 610) is precipitated by 0.1 gm. of glucose.

To use the solution, 20 cc. of the mixed solutions are placed in a flask of 250–300 cc. capacity, 80 cc. of distilled water are added, the whole thoroughly mixed and heated to boiling. On the other hand, the urine to be tested is diluted with four times its volume of water if poor in sugar, and with nine times its volume if highly saccharine (the degree of dilution required is, with a little practice, determined by the appearance of the deposit obtained in the qualitative testing); the water and urine are thoroughly mixed and a burette filled with the mixture. A little $CaCl_2$ solution is added to the Fehling's solution and the diluted urine added, in small portions toward the end, until the blue color is entirely discharged — the contents of the flask being made to boil briskly between additions from the burette. When the liquid in the flask shows no blue color when looked through with a white background in daylight the reading of the burette is taken. This reading, divided by five if the urine was diluted with four volumes of water, or by ten if with nine volumes, gives the number of cc. of urine containing 0.1 gram of glucose; and consequently the elimination of glucose in 24 hours, in decigrams, is obtained by

dividing the number of cc. of urine in 24 hours by the result obtained above.

*Example.*—20 cc. Fehling's solution used, and urine diluted with four volumes of water.

Reading of burette: 36.5 cc. $\frac{36.5}{5}=7.3$ cc. urine contain 0.1 gram glucose. Patient is passing 2,436 cc. urine in 24 hours. $\frac{2,436}{7.3}=333.6$ decigr. =33.36 grams glucose in 24 hours.

The accuracy of the determination may be controlled by filtering off some of the fluid from the flask at the end of the reaction; a portion of the filtrate is acidulated with acetic acid and treated with potassium ferrocyanid solution. If it turns reddish-brown the reduction has not been complete, and the result is affected with a plus error. To another portion of the filtrate a few drops of cupric sulfate solution are added and the mixture boiled; if any precipitation of cuprous oxid be observed, an excess of urine has been added, and the result obtained is less than the true one. But if the urine contains a large amount of urea this is decomposed with formation of ammonia, which dissolves a portion of the cupric oxid, carrying it through the filter.

This method, when carefully conducted with accurately prepared and undeteriorated solutions, is well adapted to clinical uses. The copper solution should be kept in the dark, in a well-closed bottle, and the No. II bottle should be closed with a rubber stopper. The results of the process are only accurate when the saccharine liquid contains less than 1% of glucose, and if the Fehling's solution is used in the dilution given above.

(4) *Gravimetric method.*—When more accurate results than are obtainable by Fehling's volumetric process are desired, recourse must be had to a determination of the weight of cuprous oxid obtained by reduction. A small quantity of freshly prepared Fehling's solution, diluted with four times its volume of boiled water, is heated to boiling in a small flask. To it is gradually added, with the precautions observed in the volumetric method, a known volume of the diluted urine, such that at the end of the reduction there shall remain an excess of unreduced copper salt. The alkaline fluid is separated as rapidly as possible from the precipitated oxid, by decantation and filtration through a small double filter, and the precipitate and flask repeatedly washed with hot $H_2O$ until the washings are no longer alkaline. A small portion of the precipitate remains adhering to the walls of the flask. The filter and its contents are dried and burned in a weighed porcelain crucible. When this has cooled, the flask is rinsed out with a small quantity of $HNO_3$; which is added to the contents of the crucible, evaporated over the water-bath, the crucible slowly heated to redness, cooled, and weighed. The differ-

ence between this last weight and that of the crucible + that of the filter-ash, is the weight of cupric oxid, of which 220 parts = 100 parts of glucose. Or better, the cuprie oxid is dissolved in a little dilute nitric acid, the solution evaporated with a little sulfuric acid, the residue redissolved, and the copper determined electrolytically: 175.6 Cu. = 100 glucose.

(5) *Knapp's Method.*—Several methods have been suggested, based upon the reduction of the salts of mercury. The oldest of these depends upon the reduction of mercuric cyanid by glucose. The standard solution consists of 10 gms. of pure, crystallized mercuric cyanid and 100 cc. of a solution of sodium hydroxid, sp. gr. 1.145 in a litre. Twenty cc. of this solution are reduced by 0.05 gm. of glucose. The solution is used in the same way as Fehling's solution: 20 cc. of the solution are diluted with 80 cc. of water and heated in a flask to boiling. The urine, diluted with water in the proportion of 1:4 or of 1:9, is added from a burette, at first in portions of 2 cc., then of 1 cc., then of 0.5 cc. and finally of 0.1 cc. As the end reaction is approached, the liquid clears, and the mercury deposits. A drop of liquid is then removed from time to time with a capillary tube, placed upon a piece of filter paper, and held, first over a bottle containing strong hydrochloric acid, then over one containing a strong solution of hydrogen sulfid, until it no longer assumes a yellow or brown color. The calculation is the same as with Fehling's solution, and the result is multiplied by two. The end reaction is somewhat sharper than that of Fehling's solution, and daylight is not required.

Other Sugars—*Lævulose* (fructose)—sometimes occurs in diabetic urine. When it is present the urine responds to the tests for glucose, but it either rotates to the left or has a dextrogyratory action less than that required by the result of the quantitative reduction methods.

*Lactose* occurs in the urine after the ingestion of large quantities of milk-sugar, and sometimes in the urine of women during the later stages of gestation and during lactation. Its presence may be inferred when the urine reacts with the copper and bismuth tests, but gives negative results with the fermentation test.

*Maltose* rarely acompanies glucose in pancreatic diabetes.

*Laiose* is a substance which occurs in the urine in some cases of diabetes. It is lævogyrous and amorphous, it reduces the compounds of copper and of bismuth, does not ferment, and forms a yellow or brown oily material with phenylhydrazin. It is supposed to be a sugar.

*Pentoses* (p. 264) have been met with in large amount in the urine of persons addicted to the morphin habit, in whom there is

an alternation of glycosuria and pentosuria. The pentoses are detected by Tollens' reaction: the urine is mixed with an equal volume of strong hydrochloric acid, a little phloroglucin is added, and the liquid heated by immersion in a boiling water-bath. A red-violet color indicates the presence of pentoses, galactose, lactose, or glucuronic acid. To distinguish between these the liquid is examined with the spectroscope, when, in the presence of pentoses or of glucuronic acid, a band is seen in the green, between D and E. The pentoses and glucuronic acid may be distinguished by the fusing points of their osazones, that of glucuronic acid fusing at 115°, and those of the pentoses at a higher temperature, 160°.

*Inosite*, muscle sugar, is a cyclic alcohol, $C_6H_6(OH)_6$, which occurs in traces in normal urine, and in increased amount in albuminuria, in diabetes insipidus, and after ingestion of large quantities of water.

**Acetone** — is a normal constituent of the urine in the proportion of about 0.01 gm. in 24 hours, and is a product of the metabolism of the proteins. In the normal system this amount may be increased to 0.7 in 24 hours by exclusion of carbohydrates from the diet, when acetyl-acetic acid also appears in the urine. A similar increase also occurs during starvation. This increased elimination is immediately arrested by supplying carbohydrates, but not with addition of fats to the diet, which, on the contrary, produce a further increase. Acetonuria also occurs in pathological conditions involving increased protein metabolism, as in febrile diseases when the febrile condition is prolonged, but not when it is of short duration; also in certain mental diseases, general paresis, melancholia, epilepsy; and also after chloroform narcosis. When acetonuria exists, acetone is also eliminated by the lungs, and communicates a peculiar, sweet, apple-like odor to the breath. The acetonuria of diabetes mellitus is most significant, for, not only does the simultaneous occurrence of glucose and of acetone in the urine render the diagnosis of diabetes certain, but the amount of the latter, which may reach 5 gms. in 24 hours, is directly proportionate to the intensity of the disease. The increased elimination of acetone is also in part due to the exclusion of carbohydrates from the diet of the diabetic, and both acetone and threatening symptoms disappear sometimes on addition of carbohydrates, to the extent of 50 to 100 gms. of glucose-equivalent in 24 hours, to the diet.

Probably acetone is not of itself actively poisonous, and the serious symptoms of the later stages of diabetes sometimes ascribed to it are really symptoms of "acidism" caused by the presence in the blood of acetyl-acetic acid and $\beta$-oxybutyric acid, which always accompany the acetone, and possibly of other acids as well. The

chemical relationship of these three substances is quite close, as is shown by their formulæ: acetone = $CH_3.CO.CH_3$; acetyl-acetic acid = $CH_3.CO.CH_2.COOH$, and $\beta$-oxybutyric acid = $CH_3.CHOH.CH_2.COOH$.

**Tests for Acetone.**—As acetyl-acetic acid is decomposed, with formation of acetone, by simple heating of the urine, this must first be tested for by *Gerhardt's test:* Add dilute solution of neutral ferric chlorid so long as a precipitate (of phosphates) is formed, filter, and add more ferric chlorid solution, a wine red color is produced if acetyl-acetic acid be present. If the result be affirmative it should be confirmed by: (1) Render a portion of the urine faintly acid, boil, cool, and repeat the test, which should give a negative result; (2) acidulate another portion with dilute sulfuric acid, agitate with ether, and then agitate the separated ether with dilute ferric chlorid solution, which should be colored wine-red. If there be no acetyl-acetic acid present the urine is tested for acetone as directed below, but if it be present the urine is rendered faintly alkaline, agitated in a separator with a mixture of alcohol and ether, the ether separated, agitated with water, and the water tested for acetone by the tests given below. In the absence of acetyl-acetic acid a liter of the urine is acidulated by addition of 1 gm. of phosphoric acid, and distilled; 30 cc. of distillate being collected and tested by:

(1) *Lieben's Iodoform Test.*—Add caustic soda and a little solution of iodin in potassium iodid, and warm: the odor of iodoform is produced, and a yellow, crystalline precipitate, if the quantity be sufficient. Also reacts with alcohol. Or Gunning's modification of this test, which has the advantage of not reacting with alcohol or aldehyde, may be used: An alcoholic solution of iodin and ammonia are used in place of the aqueous iodin solution, which causes the formation from acetone of iodoform and the black nitrogen iodid, which latter gradually disappears on standing, leaving the iodoform.

(2) *Legal's Nitroprussid Test.*—Add a few drops of a freshly prepared solution of sodium nitroprussid, and then KHO or NaHO solution, when, in presence of acetone, the liquid is colored ruby-red, and, on supersaturation with acetic acid, changes to purple. Paracresol gives a yellow-red color, which changes to yellow with excess of acetic acid. Creatinin gives an initial color with this test similar to that produced by acetone, but on addition of acetic acid, it turns to yellow, and slowly to green or blue. But creatinin cannot be the source of error if the urine has been distilled as above directed.

(3) *Reynold's Mercuric Oxid Test*—is based upon the property of acetone to dissolve freshly precipitated mercuric oxid. Mercuric oxid is precipitated from a solution of mercuric chlorid by addition of an

alcoholic solution of potassium hydroxid, and a portion of the distillate is added to the mixture, which is then strongly shaken and filtered. The formation of a black precipitate by addition of ammonium sulfid to the filtrate indicates that it contains dissolved mercuric oxid.

(4) *Penzold's Indigo Test.*—Add a portion of the distillate, and then NaHO solution to solution of orthonitrobenzaldehyde, prepared by making a hot saturated solution and cooling it, when, in presence of acetone, the liquid turns yellow, then green, and finally deposits indigo-blue. If chloroform be then shaken with the mixture it forms a blue solution at the bottom of the test-tube.

The principle of Lieben's reaction is utilized in the Messinger-Huppert method of quantitative determination of acetone, the amount being calculated from the quantity of iodin used in the formation of iodoform.

**Leucin and Tyrosin**—(pp. 364, 424) are not normally present in the urine. They are said to have been met with in the urine in severe cases of typhus and of variola. In yellow atrophy of the liver they are constantly present, frequently in sufficient quantity to be found in the crystalline form in the sediment, and they have also been found in like amount in many cases of acute phosphorus poisoning. To test for their presence the urine of 24 hours is precipitated with basic lead acetate and filtered; the filtrate is freed from lead by precipitation with hydrogen sulfid and filtration; the filtrate is concentrated to a syrup, washed with a little absolute alcohol, and extracted with boiling dilute alcohol containing ammonia; the ammoniacal alcoholic liquid is filtered off hot, evaporated to small bulk, and left to crystallize. Tyrosin crystallizes in bundles of fine colorless needles (*b* fig. 41), and leucin in rounded masses of varying size, consisting of closely arranged, radiating crystals, which, as they occur in urinary sediments, are yellow or brown in color (*a* fig. 41).

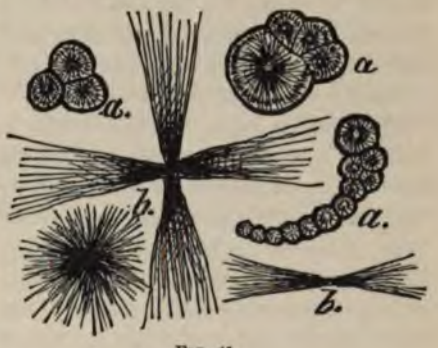



FIG. 41.

The residue may be tested for leucin by Scherer's and Hofmeister's reactions (p. 365), and for tyrosin by Piria's, Scherer's, and Hofmann's reactions (p. 425).

**Cystin**—*Dithio-diamido-dilactic acid*—(p. 367) exists in the urine normally in very small amount, and in increased quantity in the

obscure pathological condition of *cystinuria*, in which the urine also contains diamins, such as putrescin and cadaverin (p. 333), and deposits a yellowish sediment containing cystin crystals (Fig. 42), or these may be deposited to form concretions.

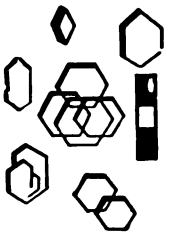


FIG. 42.

Cystin is best separated from the urine and determined by precipitation with benzoyl chlorid by Baumann and Goldmann's method, or, less exactly, by precipitation by strong acidulation with acetic acid and purification of the precipitate by reprecipitation from a solution in ammonia.

## URINARY CALCULI.

Urinary calculi, or concretions, may be formed in any part of the urinary tract, but are most frequently formed in the pelvis of the kidney or in the bladder. They are usually single, but may be multiple, as many as 300 having been found in the bladder at one time. When multiple, their surfaces are usually polished and formed into facets by mutual attrition. They vary in size from mere gravel to masses as large as a hen's egg, and weighing as much as 1,500 gms. Calculi, other than phosphatic and ammonium urate concretions, are usually composed of the same material throughout, constituting "primary deposits." Phosphatic, ammonium urate, and, very rarely, calcium carbonate calculi are produced as "secondary deposits," being formed in an alkaline or subacid urine, as a so-called "crust," which frequently constitutes almost the entire mass of the stone, by deposition upon a "nucleus," or nuclei, consisting either of a primary deposit or of some foreign substance. The constituents of urinary calculi most frequently met with are uric acid, sodium urate, ammonium urate, calcium oxalate, calcium phosphate and ammonio-magnesian phosphate; those of rarer occurrence are cystin, xanthin, urates of potassium, calcium and magnesium, and calcium carbonate. Of very exceptional occurrence are calculi of indigo, silica, fatty acids (urostealiths), and bilirubin (hæmatoidin).

Uric acid calculi are usually small in size, and of renal origin, although they are met with as vesical calculi of great size. They are always produced in a strongly acid, concentrated urine. They are gray, brownish-yellow or reddish-brown in color, sometimes smooth-surfaced, but usually finely nodulated, and quite hard. They are almost always primary, although occasionally uric acid forms alternate layers with calcium oxalate in a composite stone.

Ammonium urate is sometimes met with as a primary deposit in renal calculi in young children, which are smooth, yellow, oval

in section and relatively soft and friable. Much more frequently ammonium urate constitutes a secondary deposit.

Oxalate calculi are occasionally small and smooth, more usually very rough and coarsely nodulated, very hard, and varying in color from very pale yellow to dark-brown. They are known as "mulberry calculi" from their shape.

Phosphatic calculi are almost invariably secondary deposits, and consist usually of a mixture of calcium phosphate, ammonio-magnesium phosphate and ammonium urate. They may attain great size, are always rough-surfaced, white to yellowish or pink in color, and relatively soft and friable. Calculi whose predominating constituent is ammonio-magnesian phosphate are called "fusible calculi."

Cystin calculi, although rarely met with, are of more frequent occurrence than the other "rare" forms. They are primary, yellow, smooth or rough, of crystalline structure throughout, consisting entirely of cystin, quite soft, and usually small, although they have been known to attain the size of an egg. Xanthin calculi are of very rare occurrence. They are primary, and consist either entirely of xanthin, or of xanthin and uric acid. They vary in color from pale yellow to brown, and are sometimes as large as a pigeon's egg. Urates of potassium, calcium and magnesium are occasionally met with in urate calculi, never as the sole constituents. Calcium carbonate, while frequently met with as a secondary deposit in calculi of large size in the lower animals, is very rarely found in the human subject, in the crust of a calculus formed with a foreign body as a nucleus or in a siliceous calculus. Urostealiths consist either entirely of fatty acids with a little phosphate, or are covered with a crust of phosphates, produced as a secondary deposit. In the former case they are of the consistency of India-rubber when moist, but become hard and brittle when dry. Only five such calculi have been described. Indigo was found to be one constituent of a calculus weighing 40 gms. formed in the pelvis of a kidney. Blue crystals of indigo have also been met with inclosed in oxalate calculi. Silica calculi are extremely rare. The author has seen the nucleus of a phosphatic calculus consisting entirely of silica and an oxid of iron. An oxalate calculus has been found to contain crystals of hæmatoidin.

For the chemical examination of calculi the stone should be sawed in two, the sawdust affording sufficient material for chemical examination. The sawdust from the central portions of the calculus should be collected and examined separately from that derived from the crust. The following scheme of analysis will be found useful for the examination of calculus dust, a separate portion of the material being used for each operation, except where otherwise directed:

## SCHEME FOR DETERMINING THE COMPOSITION OF URINARY CALCULI.

1. Heat a portion on platinum foil :
   *a*. It is entirely volatile . . . . . 2
   *b*. A residue remains . . . . . 5

2. Moisten a portion with $HNO_3$; evaporate to dryness at low heat; add $NH_4HO$ :
   *a*. A red color is produced . . . . . 3
   *b*. No red color is produced . . . . . 4

3. Treat a portion with KHO, without heating :
   *a*. An ammoniacal odor [illegible]erved . . . . . *Ammonium urate.*
   *b*. No ammoniacal odor [illegible] . . . . . *Uric acid.*

4. *a*. The $HNO_3$ solution [illegible]ellow when evaporated; the yellow residue becomes [illegible]-yellow on addition of KHO, and, on heating [illegible] violet-red . . . . . *Xanthin.*
   *b*. The $HNO_3$ solution be[illegible]ark brown on evaporation, *Cystin.*

5. Moisten a portion with $HNO_3$; evaporate to dryness at low heat; add $NH_4HO$ :
   *a*. A red color is produced . . . . . 6
   *b*. No red color is produced . . . . . 9

6. Heat before the blow-pipe on platinum foil :
   *a*. Fuses . . . . . 7
   *b*. Does not fuse . . . . . 8

7. Bring into blue flame on platinum wire :
   *a*. Colors flame yellow . . . . . ***Sodium urate.***
   *b*. Colors flame violet . . . . . ***Potassium urate.***

8. The residue from 6 :
   *a*. Dissolves in dil. HCl with effervescence; the solution forms a white ppt. with ammonium oxalate . . . . . ***Calcium urate.***
   *b*. Dissolves with slight effervescence in dil. $H_2SO_4$; the solution, neutralized with $NH_4HO$, gives a white ppt. with $HNa_2PO_4$, ***Magnesium urate.***

9. Heat before the blow-pipe on platinum foil :
   *a*. It fuses . . . . . ***Ammonio-magnesian phosphate.***
   *b*. It does not fuse . . . . . 10

10. The residue from 9, when moistened with $H_2O$, is :
   *a*. Alkaline . . . . . 11
   *b*. Not alkaline . . . . . ***Tricalcic phosphate.***

11. The original substance dissolves in HCl:

*a*. With effervescence . . . . . *Calcium carbonate.*

*b*. Without effervescence . . . . . *Calcium oxalate.*

## MILK

As the milk of the cow has been the best studied, and as it is an important article of food, it will be first considered, and the difference between it and human milk will be subsequently referred to.

**Physical Properties.**—Milk is white, yellowish, or, in thin layers, or if diluted with water, bluish. It is opaque, the opacity being due to the fact that it is an emulsion, and that light is extinguished by the repeated refractions in passing between the watery liquid and the oil globules. Consequently, the richer the milk is in fat, the thinner the layer in which it is capable of causing a certain degree of extinction of light; a fact which is utilized in some forms of "milk-testers." The odor of milk is faint, but characteristic, and its taste is sweetish.

Its reaction when fresh is amphoteric, the mean alkalinity being equivalent to 41 cc. N/10 NaHO for 100 cc. milk (phenolphthaleïn), and its mean acidity equivalent to 19.5 cc. N/10 $H_2SO_4$. In air the reaction soon turns to acid, by reason of formation of lactic and succinic acids from the milk-sugar by micro-organisms, a change which takes place during the "souring" of milk, and has an influence upon the action of heat upon it. Fresh milk does not coagulate upon boiling, even after treatment with carbon dioxid. As it gradually sours, it first coagulates on boiling after treatment with $CO_2$; then on boiling alone; at a later stage it coagulates by the action of $CO_2$ at the ordinary temperature; and, finally, it coagulates spontaneously, without $CO_2$ or heat, expressing a yellowish liquid, the **whey**. This change is due to bacterial action, and may be prevented by sterilizing the milk by heat, or by antiseptics.

The specific gravity of cow's milk varies from 1027 to 1035, being higher with skimmed milk, and lower with very rich milk and with watered milk. The **lactometer** is simply a specially graduated spindle by which the sp. gr. of the milk is determined, and milk having a sp. gr. below 1027 is considered as adulterated. It must be remembered, however, that as the specific gravity is raised by skimming and lowered by watering, the original sp. gr. may be maintained by practicing both forms of adulteration to suitable degrees; and also that very rich milk has a lower sp. gr. than that less rich in cream. Therefore, the lactometer can only be relied upon when used in connection with the **creamometer**, or other means of deter-

mining the proportion of fat. The average sp. gr. of good cow's milk is 1030, and the percentage of cream 13.

**Composition.**— Milk consists of a watery solution of proteins, lactose and mineral salts, sometimes called the **plasma**, which holds in suspension minute globules of fat, sometimes called the **corpuscles**. On standing, the fat rises, more or less completely, to the surface, forming a layer much richer in fat than the milk, which is the **cream**, upon removal of which the **skim-milk** remains. The separation of fat is more rapidly and completely effected by **cream-separators**, which are centrifugal machines adapted to this purpose. The "corpuscles," which contain all the fat of the milk, number from 1 to 5½ million per cc., and are from .0024 to .0046 mm. in diameter. It is probable that the fat-globules of milk are enclosed in an envelope, because, unless the milk have been previously treated with alkali, agitation with ether does not readily extract the fat, and also because the globules are stained by certain agents which do not stain fats. Besides fat, the globules contain small quantities of lecithins, cholesterol, and a yellow coloring-matter. The fat of milk, **butter-fat**, is more complex in composition than other fats and oils, from which it differs particularly in containing a larger proportion of the glycerids of the lower, volatile, fatty acids, a fact which is taken advantage of for the detection of adulterations of butter. Milk-fat, when saponified, yields about 94% of fatty acids, of which 86 to 89% consists of insoluble, non-volatile acids, palmitic, stearic and oleic, with minute quantities of caprylic, capric, lauric and arachic acids (p. 283), the oleic acid constituting from $\frac{3}{10}$ to $\frac{4}{10}$ of the whole. The remaining 5 to 8% consist of soluble, volatile acids, butyric ($\frac{3}{7}$ to $\frac{5}{7}$) and caproic ($\frac{2}{7}$ to $\frac{3}{7}$). Other fats and oils yield only mere traces of volatile, soluble acids on saponification. Whether these acids exist in milk and butter as separate glycerids, such as tributyrin, $C_3H_5(C_4H_7O_2)_3$, tripalmitin, $C_3H_5(C_{16}H_{31}O_2)_3$, and tristearin, $C_3H_5(C_{18}H_{35}O_2)$, or as mixed glycerids, such as $C_3H_5(C_4H_7O_2)(C_{16}H_{31}O_2)(C_{18}H_{35}O_2)$, is unknown.

**Butter.**— Good, natural butter contains 80 to 90% of butter-fat, 6 to 10% of water, 2 to 5% of curd (casein), 2 to 5% of salt, and, almost always, some artificial "butter-color." About the only adulteration of butter now practiced is by admixture of other animal fats (beef or mutton tallow), and vegetable or animal oils (cotton-seed or lard-oil), or by substitution of imitation butter. **Oleomargarine** is a product made in imitation of butter, which it resembles very closely in color, taste, odor, and general appearance. It is made from beef-fat, which is hashed, steamed, and subjected to pressure at a carefully regulated temperature. Under this treatment it is separated into two fatty products, one a white solid, "stearin,"

the other a faintly yellow oil, "oleo-oil." This oil is then mixed with milk, and the remaining steps in the manufacture are the same as in making butter from cream. "Butterine," "suine," etc., are products made, by modifications of the above process, from beef or mutton-tallow, lard and cotton-seed oil.

**Milk-plasma**—the liquid portion of the milk remaining after complete removal of the fat-globules, contains the dissolved constituents. These consist of at least three proteins: Caseinogen, the parent substance from which the casein is derived, lactalbumin, and lactoglobulin; two carbohydrates, milk sugar and dextrine-like substance; mineral salts; and small quantities of lecithins, nuclein, cholesterol, urea, creatin, creatinin, and calcium citrate.

**Casein**—is the protein produced from the caseinogen of milk by the coagulating action of the rennet from the stomach of the calf. Probably the caseinogens, and the caseins derived therefrom, in the milk of different kinds of animals are not identical with each other. That from human milk and that from the milk of the cow differ in the form of the coagulum, in solubility in acids, and in the nature of the products of decomposition. The casein of cow's milk is a nucleoalbumen, and, on digestion with pepsin and hydrochloric acid, leaves a pseudonuclein, which is not the case with the casein from human milk. It contains 0.8% of sulfur, and 0.85% of phosphorus. Casein, which is the principal protein of cheese, is, when dry, a white powder, very sparingly soluble in water and in solutions of neutral salts, except that it is somewhat soluble in 1% solutions of sodium fluorid or of potassium or ammonium oxalate. It behaves as an acid towards alkaline solutions, in which it dissolves, forming solutions which may be neutral or even acid, if the proportion of alkali be small. It expels carbon dioxid from calcium carbonate, and forms a soluble compound with calcium phosphate. Its solutions do not coagulate by heat. Addition of a very small quantity of dilute hydrochloric or acetic acid causes precipitation of casein from its solutions, less readily in the presence of neutral salts; the precipitate dissolving readily in an excess of the acid, and being again produced by marked excess of mineral acids. Neutral solutions are precipitated by salting with sodium chlorid or magnesium sulfate, and by solutions of alum, or of zinc or copper salts. The most notable property of caseinogen is its coagulation (conversion into casein or paracasein) by the action of rennet (chymosin), in the presence of calcium salts. Chymosin alone causes a change in caseinogen, but not coagulation; for if a solution of caseinogen be treated with chymosin no coagulation occurs, but if the chymosin be then destroyed by heat, a coagulum is formed by addition of a calcium salt.

On digestion with pepsin-hydrochloric acid, cow's casein dissolves, leaving a residue of a nucleoalbumen, whose quantity and whose phosphorus-content vary. Indeed, with a large excess of pepsin-hydrochloric acid, no residue remains. By tryptic digestion the phosphorus is split off, in part as phosphoric acid, and in part in organic combination.

Casein may be obtained from milk by dilution with four volumes of water, precipitation by addition of acetic acid to 1 p/m, repeated resolution in dilute alkali and reprecipitation by acetic acid, washing with water, drying, and washing with alcohol, and finally with ether.

**Lactalbumin**—is a protein containing no phosphorus, and 1.73% of sulfur. It has the properties of the albumins, and resembles serum albumin, having about the same coagulation-temperature, 72° to 84°, varying with the proportion of salts present, but having a lower specific rotary power: $[a]_D = -37°$. It may be separated from milk, after removal of lactoglobulin and casein by salting with magnesium sulfate, by precipitation with acetic acid.

**Lactoglobulin**—closely resembling, if not identical with serum globulin, is a protein precipitable from milk, after removal of casein by salting with sodium chlorid, by saturation with magnesium sulfate.

**Lactose**—see p. 272.

**Mineral salts**—exist in cow's milk in the proportion of about 0.7%. They consist of the chlorids and phosphates of sodium, potassium, calcium and magnesium, and traces of iron.

Human milk—differs from cow's milk principally in the proportion of the several constituents, and in the nature of the proteins. The composition of cow's milk and of human milk is given by König as follows:

| | Cow's Milk | | | Human Milk | | |
|---|---|---|---|---|---|---|
| | Mean | Minimum | Maximum | Mean | Minimum | Maximum |
| Water | 87.41 | 80.32 | 91.50 | 87.21 | 83.69 | 90.90 |
| Total solids | 11.59 | 8.50 | 19.68 | 12.71 | 9.10 | 16.31 |
| Fat | 3.66 | 1.15 | 7.09 | 3.78 | 1.71 | 7.60 |
| Milk-sugar | 4.92 | 3.20 | 5.67 | 6.04 | 4.11 | 7.80 |
| Casein | 3.01 | 1.17 | 7.40 | 1.03 | 0.18 | 1.90 |
| Albumin | 0.75 | 0.21 | 5.04 | 1.26 | 0.39 | 2.35 |
| Proteins | 3.76 | 1.38 | 12.44 | 2.29 | 0.57 | 4.25 |
| Ash | 0.70 | 0.50 | 0.78 | 0.31 | 0.14 | ? |

Therefore, in human milk the proportion of proteins is less, and that of sugar greater than in cow's milk.

The casein of human milk is, apparently, not a nucleoalbumen,

at all events it leaves no residue of pseudonuclein on digestion with pepsin-hydrochloric acid. It does, however, contain phosphorus in somewhat less proportion than cow's casein, 0.68%. It is coagulated incompletely by rennet in fine, separate flocculi, while cow's casein is coagulated by rennet in dense, curdy masses. Human casein is more difficultly precipitated by acids than cow's casein, and is more readily soluble in slight excess of the acid. These differences are not due to differences in the nature or amount of the salts present, but to differences in the proteins themselves, which also differ in their chemical composition, human casein containing less carbon, nitrogen and phosphorus than cow's casein, and more hydrogen, oxygen and sulfur. The spontaneous coagulation of human milk on exposure to air at the ordinary temperature takes place more slowly than that of cow's milk. The quantity of proteins in human milk is notably greater early in lactation than later, being as high as 3 p/m in the earlier stages. The proportion of milk-sugar, on the contrary, increases with the duration of lactation.

Besides caseinogen, lactalbumin and lactoglobulin, human milk contains another protein, **opalisin,** which contains a large proportion of sulfur, 4.7%.

**Abnormal Milk.**—It will be seen by the table on page 624 that the proportion of fat, sugar and proteins in both cow's milk and human milk vary within quite wide limits. A milk containing less than the minimum of these constituents there given is certainly abnormal, and one containing no more than the mean is of inferior quality. The New York state dairy law declares any milk found on analysis to contain "less than 12% of milk solids, which shall contain not less than 3% of fat" to be adulterated. These limits are fixed upon the assumption, based upon a great number of analyses, that a milk falling below the requirements, if not fraudulently adulterated, is the product of cows kept under improper hygienic conditions, or diseased. The quality of milk, whether of women or of cows, is affected by the physical condition of the individual, the nutrition, and the composition of the food, the duration of lactation, and the mental emotions. The last-named influence the quality of the milk much more seriously than is generally appreciated. The milk of cows which are harassed or excited has been found to be much more liable to cause alimentary disturbances in infants than that obtained from animals which are gently treated and kept free from excitement. It is also well known that the milk of women during violent mental excitement may become absolutely poisonous to the nursing infant.

Cow's milk has been frequently the medium of transmission of disease. Bacteria are found in the freshly-drawn milk of cows

affected by disease, and it has been stated that tuberculosis may thus be transmitted from the cow to the human subject. Less open to question is the transmission of diphtheria, scarlet fever, and, particularly, typhoid, by contamination of the milk by exposure to the air, or by admixture of contaminated water, particularly as milk is an excellent nutrient material for bacteria. The physical qualities of milk are also sometimes modified by bacterial action, the milk becoming bitter in taste, or ropy in consistency, or red or blue in color.

Medicinal and poisonous substances taken by the mother may pass into the milk in quantity sufficient to cause serious effects upon the nursing infant. Thus infants are frequently narcotized by opiates taken by the mother, and at least two instances of fatal poisoning by this means have been reported.

The adulteration of milk now is practically limited to the addition of water, or the removal of cream, or both.

**Analysis of Milk.**—The constituents of milk usually determined in milk analysis are: total solids (milk-solids), fat, solids not fat, and ash. A simple method, and one giving sufficiently accurate results, is that of Sharples: ten cc. of the milk are measured out into a weighed, flat platinum dish (milk-dish), and weighed. The difference between this weight and that of the dish is the weight of milk used. The dish is then placed on the water-bath until the milk is evaporated to dryness, heated for half an hour in an air-oven at 105°, cooled and weighed. This weight, minus the weight of the dish, is the weight of milk-solids in the weight of milk used. The dish is then filled with petroleum-ether (obtained by distilling gasolene on the water-bath), which is poured off from the solid residue, which usually adheres firmly to the dish; and the treatment with petroleum-ether repeated six times. The residue is heated for a few minutes in the air-oven, cooled, and weighed. This weight, minus that of the empty dish, is that of the solids not fat; and, subtracted from the weight of milk-solids, gives the weight of fat in the amount of milk used. The residue is then burnt to a white ash, cooled and weighed, giving the amount of ash.

The extraction of fat by the above method is not complete, and therefore the determination of fat is affected with a slight minus error. When more accurate determination of fat is desired, Adams' method is to be preferred: strips of thin blotting-paper about 50 cent. long and 6 cent. wide, which have been freed from fat by extraction with ether and with alcohol, dried and weighed, along with the platinum wire below referred to, are used. The milk sample is placed in a small wash-bottle, which is then weighed. One of the paper strips is suspended in a horizontal position, and from

8 to 10 cc. of the milk are distributed over it from the wash-bottle, which is then reweighed to determine the amount of the sample used. When the milk upon the paper strip has become air-dried, the strip is coiled into a spiral, about which the platinum wire is fastened, and which is then dried in an air-oven at 105°. When dry, the spiral is cooled and weighed, to determine the total solids, and then extracted with ether in a Soxhlet extractor. The fat is determined by evaporation of the ether extract, and weighing the residue.

Of the more rapid, physical methods of fat-determination probably the most satisfactory is that of Babcock: The milk is mixed with an equal volume of sulfuric acid, transferred to a small bottle having a long, thin, graduated neck, constructed for the purpose, and rotated in a centrifugal. The percentage of fat is read off on the graduation.

For the determination of total proteins and sugar in the same sample, Ritthausen's method is generally used: 25 gm. of the milk are diluted with water to 400 cc., 10 cc. of a solution of $CuSO_4$ containing 6.5 gm. to the litre, and a solution of KHO (14.2 gm. to the litre), or of NaHO (10.2 gm. to the litre) are added so that the reaction remains faintly acid or neutral (it must not become alkaline). When the precipitate of proteins has formed, 100 cc. of water are added, the mixture is stirred and filtered through a small filter of known nitrogen-content. The filtrate is used for the sugar determination: 100 cc. are added to 50 cc. of boiling Fehling's solution, and the determination is concluded as usual. The protein coagulum is washed, by decantation and upon the filter, with water, and the proportion of nitrogen is determined in the filter and precipitate by Kjeldahl's method. The nitrogen found, multiplied by 6.37, gives the protein-content.

# APPENDIX.

# APPENDIX A.

## ORTHOGRAPHY AND PRONUNCIATION OF CHEMICAL TERMS.

In 1887 a committee was appointed by the American Association for the Advancement of Science, to consider the question of securing uniformity in the spelling and pronunciation of chemical terms. The work of this committee extended through the four following years. As a result of widespread correspondence and detailed discussion at the annual meetings of the Chemical Section of the American Association, the following rules have been formulated and adopted by the Association.

A circular embodying the substance of these rules has been issued by the Bureau of Education at Washington, and distributed among chemists and teachers of chemistry, with a recommendation of their general adoption.

### GENERAL PRINCIPLES OF PRONUNCIATION.

1. The pronunciation is as much in accord with the analogy of the English language as possible.
2. Derivatives retain as far as possible the accent and pronunciation of the root word.
3. Distinctly chemical compound words retain the accent and pronunciation of each portion.
4. Similarly sounding endings for dissimilar compounds are avoided, hence -ĭn, -ĭd, -īte, -āte.

### ACCENT.

In polysyllabic chemical words the accent is generally on the antepenult; in words where the vowel of the penult is followed by two consonants, and in all words ending in -ic, the accent is on the penult.

### PREFIXES.

All prefixes in strictly chemical words are regarded as parts of compound words, and retain their own pronunciation unchanged (as ă′ceto-, ă′mĭdo-, ă′zo-, hȳ′dro-, ī′so-, nī′tro-, nītrō′so-).

ELEMENTS.

**In words ending in -ium, the vowel of the antepenult is short if i (as ĭrĭ′dium), or y (as dĭdў′mium), or if before two consonants (as că′lcium), but long otherwise (as tĭtā′nium, sĕlē′nium, chrō′mium).**

| | | | |
|---|---|---|---|
| alū′minium | e′rbium | me′rcury | so′dium |
| a′ntimony | flŭ′orĭn | mŏlў′bdenum | stro′ntium |
| a′rsĕnic | gă′llium | nĭ′ckel | (shium) |
| bā′rium | germā′nium | nĭ′trogen | sŭ′lfur |
| bĭ′smuth (biz) | glu′cinum | ō′smium | tă′ntalum |
| bō′ron | gold | ō′xygen | tellū′rium |
| brō′mĭn | hў′drogen | palla′dium | te′rbium |
| că′dmium | ĭ′ndium | phŏs′phorus | thă′llium |
| că′lcium | ĭ′odĭn | plă′tinum | thō′rium |
| ca′rbon | ĭrĭ′dium | potă′ssium | tĭn |
| cē′rium | iron | rhō′dium | tĭtă′nium |
| cē′sium | lă′nthanum | rubĭ′dium | tŭ′ngsten |
| chlō′rĭn | lead | ruthē′nium | ūrā′nium |
| chrō′mium | lĭ′thium | samā′rium | vănā′dium |
| cō′balt | magnē′sium | scă′ndium | ytte′rbium |
| colŭ′mbium | (shium) | sĕlē′nium | ў′ttrium |
| co′pper | ma′nganese | sĭ′licon | zinc |
| dĭdў′mium | (ese) | silver | zirco′nium |

Also: ămmō′nium, phosphō′nium, hă′logen, cўă′nogen, ămĭ′dogen.

Note in the above list the spelling of the halogens, cesium and sulfur; f is used in the place of ph in all derivatives of sulfur (as sulfuric, sulfite, sulfo-, etc.).

## TERMINATIONS IN -ic.

The vowel of the penult in polysyllables is short (as cўă′nic, fūmă′ric, arsĕ′nic, silĭ′cic, ĭŏ′dic, būtў′ric), except (1) u when not used before two consonants (as mercū′ric, prū′ssic), and (2) when the penult ends in a vowel (as benzō′ic, olē′ic); in dissyllables it is long except before two consonants (as bō′ric, clĭ′tric). Exception: acē′tic or ăcĕ′tic.

The termination -ic, is used for metals only where necessary to contrast with -ous (thus avoid aluminic, ammonic, etc.).

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Fāte, făt, fär, mēte, mĕt, pīne, pĭn, marine, nōte, nŏt, mōve, tūbe, tŭb, rūle, mў, ў = ĭ.

′ Primary accent; ″ secondary accent. N. B.—The accent follows the vowel of the syllable upon which the stress falls, but does not indicate the division of the word into syllables.

### TERMINATIONS IN ous.

The accent follows the general rule (as plă′tinous, sŭ′lfurous, phŏ′sphorous, coba′ltous). Exception: acē′tous.

### TERMINATIONS IN -ate AND -ite.

The accent follows the general rule (as ă′cetāte, vă′nadāte): in the following words the accent is thrown back: ă′bietāte, ă′lcoholāte, ă′cetonāte, ă′ntimonīte.

### TERMINATIONS IN -id (FORMERLY -ide).

The final e is dropped in every case and the syllable pronounced ĭd (as chlō′rĭd, ī′odĭd, hȳ′drĭd, ŏ′xĭd, hȳdrŏ′xĭd, sŭ′lfĭd, ă′mĭd, ă′nilĭd, mūrĕ′xĭd).

### TERMINATIONS IN -ane, -ene, -ine, AND -one.

The vowel of these syllables is invariably long (as mĕ′thāne, ĕ′thāne, na′phthalēne, a′nthracēne, prō′pīne, quĭ′nōne, ă′cetōne, kē′tōne).

A few dissyllables have no distinct accent (as benzēne, xȳlēne, cētēne).

The termination -ine is used only in the case of doubly unsaturated hydrocarbons, according to Hofmann's grouping (as propīne).

### TERMINATIONS IN -in.

In names of chemical elements and compounds of this class, which includes all those formerly ending in -ine (except doubly unsaturated hydrocarbons), the final e is dropped, and the syllable pronounced -in (as chlō′rĭn, brō′mĭn, etc., ă′mĭn, ă′nilĭn, mo′rphĭn, quĭ′nĭn (kwĭ′nĭn), vanĭ′llĭn, alloxă′ntĭn, absi′nthĭn, emŭ′lsĭn, că′ffeĭn, cō′caĭn).

### TERMINATIONS IN -ol.

This termination, in the case of specific chemical compounds, is used *exclusively* for alcohols (and phenols, W.), and when so used is

---

Fāte, făt, făr, mēte, mĕt, pīne, pĭn, marīne, nōte, nŏt, möve, tūbe, tŭb, rüle, mȳ, ȳ = ĭ.

′ Primary accent; ″ secondary accent. N. B.—The accent follows the vowel of the syllable upon which the stress falls, but does not indicate the division of the word into syllables.

never followed by a final e. The last syllable is pronounced -ōl (as gly′cōl, phē′nōl, crē′sōl, thȳ′mōl (ti), glȳ′cerol, quĭ′nōl.) Exceptions: ă′lcohŏl, a′rgŏl.

### TERMINATIONS IN -ole.

This termination is always pronounced -ōle, and its use is limited to compounds which are not alcohols (or phenols, W.) (as ĭ′ndōle).

### TERMINATIONS IN -yl.

No final e is used; the syllable is pronounced ȳl (as ă′cetȳl, ă′mȳl, cē′rotȳl, cē′tȳl, ĕ′thȳl).

### TERMINATIONS IN -yde.

The y is long (as ă′ldehȳde).

### TERMINATIONS IN -meter.

The accent follows the general rule (as hydrŏ′meter, barŏ′meter, lactŏ′meter). Exception: words of this class used in the metric system are regarded as compound words, and each portion retains its own accent (as cĕ′ntime″ter, mi′llime″ter, kĭ′lome″ter).

### MISCELLANEOUS WORDS WHICH DO NOT FALL UNDER THE PRECEDING RULES.

Note the spelling: albumen, albuminous, albuminiferous, asbestos, gramme, radical.

Note the pronunciation: a′lkalīne, a′lloy (n. and v.), a′llotropy, a′llotropism, ī′somerism, pŏ′lymerism, apparā′tus (sing. and plu.), āqua regia, barȳ′ta, cĕntigrade, co′ncentrated, crystallĭn or crystallīne, electrŏ′lysis, lĭter, mŏ′lecule, mŏlĕ′cular, nō′menclā″ture, olē′fiant, vā′lence, ū′nivā″lent, bī′vā″lent, trī′vā″lent, qua′drivā″lent, tĭ′trate.

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Fāte, făt, fâr, mēte, mĕt, pīne, pĭn, marīne, nōte, nŏt, möve, tūbe, tŭb, rūle, mў, ў = ĭ.

′ Primary accent; ″ secondary accent. N. B.—The accent follows the vowel of the syllable upon which the stress falls, but does not indicate the division of the word into syllables.

## A LIST OF WORDS WHOSE USE SHOULD BE AVOIDED IN FAVOR OF THE ACCOMPANYING SYNONYMS.

| *For* — | *Use* — |
|---|---|
| sodic, calcic, zincic, nickelic, etc., chlorid, etc. | sodium, calcium, zinc, nickel, etc., chlorid, etc. (vid. terminations in -ic supra). |
| arsenetted hydrogen | arsin |
| antimonetted hydrogen | stibin |
| phosphoretted hydrogen | phosphin |
| sulfuretted hydrogen, etc. | hydrogen sulfid, etc. |

| *For* — | *Use* — |
|---|---|
| beryllium | glucinum |
| niobium | columbium |
| glycerin | glycerol |
| hydroquinone (and hydrochinon) | quinol |
| pyrocatechin | catechol |
| resorcin, etc. | resorcinol, etc. |
| mannite | mannitol |
| dulcite, etc. | dulcitol, etc. |
| benzol | benzene |
| toluol, etc. | toluene, etc. |
| thein | caffein |

| *For* — | *Use* — |
|---|---|
| furfurol | furfuraldehyde |
| fucusol | fucusaldehyde |
| anisol | methyl phenate |
| phenetol | ethyl phenate |
| anethol | methyl allylphenol |
| alkylogens | alkyl haloids |
| titer (n.) | strength or standard |
| titer (v.) | titrate |
| monovalent | univalent |
| divalent, etc. | bivalent, etc |
| quantivalence | valence |

# APPENDIX B.—TABLES.

## TABLE I.—SOLUBILITIES.

### FRESENIUS.

W or w = soluble in $H_2O$. A or a = insoluble in $H_2O$; soluble in HCl, $HNO_3$, or aqua regia. I or i = insoluble in $H_2O$ and acids. W–A = sparingly soluble in $H_2O$, but soluble in acids. W–I = sparingly soluble in $H_2O$ and acids. A–I = insoluble in $H_2O$, sparingly soluble in acids. Capitals indicate common substances.

| | Aluminium. | Ammonium. | Antimony. | Barium. | Bismuth. | Cadmium. | Calcium. | Chromium. | Cobalt. | Copper. | Ferrous. | Ferric. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Acetate | W | W | .. | W | w | w | W | w | w | W | w | W |
| Arsenate | a | w | a | a | a | a | a | a | a | a | a | a |
| Arsenite | .. | w | a | a | .. | .. | a | .. | a | A | a | a |
| Benzoate | w | w | .. | w | .. | w | w | .. | .. | a | w | a |
| Borate | a | w | .. | a | a | w–a | a | a | a | a | a | a |
| Bromid | w | W | w–a | w | w–a | w | w | w–i | w | w | w | w |
| Carbonate | a | W | .. | A | A | a | A | a | A | A | A | a |
| Chlorate | w | w | .. | W | w | w | w | w | w | w | w | w |
| Chlorid | w | W[2] | W–A[6] | W | W–A[10] | W | W | W–I | W | W | W | W |
| Chromate | .. | w | a | a | a | a | w–a | a | a | w | .. | w |
| Citrate | w | w | .. | a | .. | a | w–a | w | w | w | w | W |
| Cyanid | .. | w | .. | w–a | .. | a | w | a | a–i | a | a–i | .. |
| Ferricyanid | .. | w | .. | .. | .. | .. | w | .. | i | .. | I | w |
| Ferrocyanid | .. | w | .. | w–a | .. | .. | w | .. | i | i | i | I |
| Fluorid | w | W | w | a–i | w | w–a | A | w | w–a | a | w–a | w |
| Formate | w | w | .. | w | w | w | w | w | w | w | w | w |
| Hydrate | A | W | A | W | a | a | W–A | A | A | a | a | A |
| Iodid | w | W | w–a | w | a | W | w | w | w | w | W | w |
| Malate | w | w | .. | w–a | .. | .. | w–a | .. | .. | .. | .. | w |
| Nitrate | w | W | .. | W | W[11] | w | w | W | W | W | W | W |
| Oxalate | a | W | a | a | a | a | A | w–a | A | a | a | a |
| Oxid | A–I | .. | a[7] | W | a | a | W–A | A–I | A | A | a | A |
| Phosphate | a | W[3] | w–a | w–a | a | a | W–A | a | a | a | a | a |
| Silicate | A–I | .. | .. | a | .. | a | a | a | a | a | a | a |
| Succinate | w a | w | .. | w–a | .. | w | w–a | .. | w–a | w–a | w | .. |
| Sulfate | W[1] | W[4] | a | A | w | W | W–I | W–A[12] | W[13] | W | W | W |
| Sulfid | a | W | A[8] | W | a | A | W–A | a–i | a | A | A | A |
| Tartrate | w | w[5] | a[9] | a | a | w–a | a | w | w | w | w–a | W[14] |

[1] $(Al_2)(NH_4)_2(SO_4)_4$=W; $(Al_2)K_2(SO_4)_4$=W. [2] $As(NH_4)Cl_4$=W; $Pt(NH_4)Cl_5$=W–I. [3] $HNa(NH_4)PO_4$=W; $Mg(NH_4)PO_4$=A. [4] $Fe(NH_4)_2(SO_4)_2$=W; $Cu(NH_4)_2(SO_4)_2$=W. [5] $C_4H_4O_6K(NH_4)$=W. [6] SbOCl=A. [7] $Sb_2O_3$=soluble in HCl, not in $HNO_3$. [8] $Sb_2S_3$=sol. in hot HCl, slightly in $HNO_3$. [9] $C_4H_4O_6K(SbO)$=W. [10] BiOCl=A. [11] $(BiO)NO_3$=A. [12] $(Cr_2)K_2(SO_4)_4$=W. [13] CoS=easily sol. in $HNO_3$, very slowly in HCl. [14] $(C_4H_4O_6)_4(Fe_2)K_2$=W.

**TABLE I.—SOLUBILITIES.—Continued.**

FRESENIUS.

W or w = soluble in $H_2O$. A or a = insoluble in $H_2O$; soluble in HCl, $HNO_3$, or aqua regia. I or i = insoluble in $H_2O$ and acids. W–A = sparingly soluble in $H_2O$, but soluble in acids. W–I = sparingly soluble in $H_2O$ and acids. A–I = insoluble in $H_2O$, sparingly soluble in acids. Capitals indicate common substances.

| | Lead. | Magnesium. | Manganese. | Mercurous. | Mercuric. | Nickel. | Potassium. | Silver. | Sodium. | Strontium. | Stannous. | Stannic. | Zinc. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Acetate . . | W | w | w | w–a | w | w | W | w | W | w | w | w | W |
| Arsenate . | a | a | a | a | a | a | W | a | W | a | a | a | . . |
| Arsenite . . | a | a | a | a | a | a | w | a | w | a | a | . . | . . |
| Benzoate . | a | w | w | a | w–a | . . | w | w–a | w | . . | . . | . | . . |
| Borate . . . | a | w–a | a | . . | . . | a | W | a | W | a | a | . . | a |
| Bromid . . . | w–i | w | w | a–i | w | w | W | a | W | w | . . | . . | w |
| Carbonate . | A | A | A | a | a | A | W | a | W | A | . . | . . | A |
| Chlorate . . | w | w | w | w | w | w | W | w | w | w | w | . . | w |
| Chlorid . . . | W–I | W | W | A–I | W[16] | W | W[20] | I | W | W | W | W | W |
| Chromate . . | A–I | w | w | a | w–a | a | W | a | w | w–a | a | . . | w |
| Citrate . . . | a | w | a | a | w–a | w | w | a | W | a | . . | . . | w–a |
| Cyanid . . | a | w | a | . . | W | a–i | W | i | w | w | . . | . . | a |
| Ferricyanid | w–a | w | i | . . | . . | i | W | i | w | . . | . . | . . | a |
| Ferrocyanid | a | w | a | . . | . | i | W | i | w | w | . . | . . | a–i |
| Fluorid . . . | a | a–i | a | . | w–a | w–a | w | w | w | a–i | w | w | w–a |
| Formate . . | w–a | w | w | w | w | w | w | w | w | w | w | . . | w |
| Hydrate . . | a | A | a | . . | . . | a | W | . . | W | w | a | a | a |
| Iodid . . . . | W–A | w | w | A | A | w | W | i | w | w | w | w | w |
| Malate . . . | w–a | w | w | a | w–a | . | w | w–a | w | w | w | w | w |
| Nitrate . . . | W | w | w | W | W | W | W | W | W | W | . . | . . | w |
| Oxalate . . . | a | a | w–a | a | a | a | W | a | W | a | a | w | a |
| Oxid . . . . | A | A | A[15] | A | A | A | W | a | W | W | a | A–I | A |
| Phosphate . | a | a[3] | a | a | a | a | w | a | W | a | a | a | a |
| Silicate . . | a | a | a | . . | . . | a | W | . . | W | a | . | . . | a |
| Succinate . . | a | w | w | a | w–a | w | w | a | w | w–a | . | a | w–a |
| Sulfate . . . | A–I | W | W | w–a | W[17] | W | W[12] | W–A | W | I | w | . | W |
| Sulfid . . . | A | a | a | a | A[18] | A[19] | W | a[21] | W | w | a[22] | A[22] | A[23] |
| Tartrate . . | a | w–a | w–a | w–a | a | a | W | a | w | a | a | . . | a |

[15] $MnO_2$ = sol. in HCl; insol. in $HNO_3$. [16] Mercurammonium chlorid = A. [17] Basic sulfate = A. [18] HgS = insol. in HCl and in $HNO_3$, sol. in aqua regia. [19] See 13. [20] $PtKCl_5$ = W–A. [21] Only soluble in $HNO_3$. [22] Sn sulfids = sol. in hot HCl; oxidized, not dissolved, by $HNO_3$. Sublimed $SnCl_4$ only sol. in aq. regia. [23] Easily sol. in $HNO_3$, difficultly in HCl.

$Au_2S$ = insol. in HCl and in $HNO_3$, sol. in aq. regia. $AuBr_3$, $AuCl_3$, and $Au(CN)_3$ = w; $AuI_3$ = a $PtS_2$ = insol. in HCl, slightly sol. in hot $HNO_3$; sol. in aq. regia. $PtBr_4$, $PtCl_4$, $Pt(CN)_4$, $Pt(NO_3)_4$, $Pt(C_2O_4)_2$, $Pt(SO_4)_2$ = w; $PtO_2$ = a; $PtI_4$ = i.

## TABLE II.—WEIGHTS AND MEASURES.

### MEASURES OF LENGTH.

1 millimeter = 0.001 meter = 0.0394 inch.
1 centimeter = 0.01 " = 0.3937 "
1 decimeter = 0.1 " = 3.9371 inches.
**1 METER** = 39.3708 "
1 decameter = 10 meters = 32.8089 feet.
1 hectometer = 100 " = 328.089 "
1 kilometer = 1000 " = 0.6214 mile.

| Inch. | | Millimeters. | Inches. | | Centimeters. | Inches. | | Centimeters. |
|---|---|---|---|---|---|---|---|---|
| [illegible] | = | 0.3819 | 2 | = | 5.08 | 9 | = | 22.86 |
| [illegible] | = | 0.7637 | 3 | = | 7.62 | 10 | = | 25.40 |
| [illegible] | = | 1.5875 | 4 | = | 10.16 | 11 | = | 27.94 |
| [illegible] | = | 3.175 | 5 | = | 12.70 | 12 | = | 30.48 |
| [illegible] | = | 6.35 | 6 | = | 15.24 | 18 | = | 45.72 |
| [illegible] | = | 12.7 | 7 | = | 17.78 | 24 | = | 60.96 |
| 1 | = | 25.4 | 8 | = | 20.32 | 36 | = | 91.44 |

### MEASURES OF CAPACITY.

1 milliliter = 1 c.c. = 0.001 liter = 0.0021 U. S. pint.
1 centiliter = 10 " = 0.01 " = 0.0211 " "
1 deciliter = 100 " = 0.1 " = 0.2113 " "
**1 LITER** = 1000 " = 1.0567 " quart.
1 decaliter = 10 liters = 2.6418 " galls.
1 hectoliter = 100 " = 26.418 " "
1 kiloliter = 1000 " = 264.18 " "

| m. | c.c. | m. | c.c. | m. | c.c. | Fl ℥ | c.c. |
|---|---|---|---|---|---|---|---|
| 1 | = 0.06 | 26 | = 1.60 | 51 | = 3.14 | 5 | = 147.81 |
| 2 | = 0.12 | 27 | = 1.66 | 52 | = 3.20 | 6 | = 177.39 |
| 3 | = 0.19 | 28 | = 1.73 | 53 | = 3.26 | 7 | = 206.96 |
| 4 | = 0.25 | 29 | = 1.79 | 54 | = 3.32 | 8 | = 236.53 |
| 5 | = 0.31 | 30 | = 1.85 | 55 | = 3.39 | 9 | = 266.10 |
| 6 | = 0.37 | 31 | = 1.91 | 56 | = 3.46 | 10 | = 295.68 |
| 7 | = 0.43 | 32 | = 1.98 | 57 | = 3.52 | 11 | = 325.25 |
| 8 | = 0.49 | 33 | = 2.04 | 58 | = 3.58 | 12 | = 354.82 |
| 9 | = 0.55 | 34 | = 2.10 | 59 | = 3.64 | 13 | = 384.40 |
| 10 | = 0.62 | 35 | = 2.16 | 60 | = 3.70 | 14 | = 413.97 |
| 11 | = 0.68 | 36 | = 2.22 | | | 15 | = 443.54 |
| 12 | = 0.74 | 37 | = 2.28 | Fl ℥. | | 16 | = 473.11 |
| 13 | = 0.80 | 38 | = 2.34 | 1 | = 3.70 | O. | Litres. |
| 14 | = 0.86 | 39 | = 2.40 | 2 | = 7.39 | 1 | = 0.47 |
| 15 | = 0.92 | 40 | = 2.46 | 3 | = 11.09 | 2 | = 0.95 |
| 16 | = 0.99 | 41 | = 2.52 | 4 | = 14.79 | 3 | = 1.42 |
| 17 | = 1.05 | 42 | = 2.58 | 5 | = 18.48 | 4 | = 1.89 |
| 18 | = 1.11 | 43 | = 2.66 | 6 | = 22.18 | 5 | = 2.36 |
| 19 | = 1.17 | 44 | = 2.72 | 7 | = 25.88 | 6 | = 2.84 |
| 20 | = 1.23 | 45 | = 2.77 | 8 | = 29.57 | 7 | = 3.31 |
| 21 | = 1.29 | 46 | = 2.84 | Fl ℥. | | 8 | = 3.79 |
| 22 | = 1.36 | 47 | = 2.90 | 1 | = 29.57 | 9 | = 4.26 |
| 23 | = 1.42 | 48 | = 2.96 | 2 | = 59.14 | 10 | = 4.73 |
| 24 | = 1.48 | 49 | = 3.02 | 3 | = 88.67 | 11 | = 5.20 |
| 25 | = 1.54 | 50 | = 3.08 | 4 | = 118.24 | 12 | = 5.67 |

## WEIGHTS.

| | | | |
|---|---|---|---|
| 1 milligram | = 0.001 gram | = | 0.015 grain Troy. |
| 1 centigram | = 0.01 " | = | 0.154 " " |
| 1 decigram | = 0.1 " | = | 1.543 grains " |
| 1 GRAM | | = | 15.432 " " |
| 1 decagram | = 10 grams | = | 154.324 " " |
| 1 hectogram | = 100 " | = | 0.268 lb. " |
| 1 kilogram | = 1000 " | = | 2.679 lbs. " |

| Grains. | Grams. |
|---|---|
| 1/64 | = 0.001 |
| 1/32 | = 0.002 |
| 1/16 | = 0.004 |
| 1/8 | = 0.008 |
| 1/4 | = 0.016 |
| 1/2 | = 0.032 |
| 1 | = 0.065 |
| 2 | = 0.130 |
| 3 | = 0.194 |
| 4 | = 0.259 |
| 5 | = 0.324 |
| 6 | = 0.389 |
| 7 | = 0.454 |
| 8 | = 0.518 |
| 9 | = 0.583 |
| 10 | = 0.648 |
| 11 | = 0.713 |
| 12 | = 0.778 |
| 13 | = 0.842 |
| 14 | = 0.907 |
| 15 | = 0.972 |
| 16 | = 1.037 |
| 17 | = 1.102 |
| 18 | = 1.166 |
| 19 | = 1.231 |
| 20 | = 1.296 |

| Grains. | Grams. |
|---|---|
| 21 | = 1.361 |
| 22 | = 1.426 |
| 23 | = 1.458 |
| 24 | = 1.555 |
| 25 | = 1.620 |
| 26 | = 1.685 |
| 27 | = 1.749 |
| 28 | = 1.814 |
| 29 | = 1.869 |
| 30 | = 1.944 |
| 31 | = 2.009 |
| 32 | = 2.074 |
| 33 | = 2.139 |
| 34 | = 2.204 |
| 35 | = 2.268 |
| 36 | = 2.332 |
| 37 | = 2.397 |
| 38 | = 2.462 |
| 39 | = 2.527 |
| 40 | = 2.592 |
| 41 | = 2.657 |
| 42 | = 2.722 |
| 43 | = 2.787 |
| 44 | = 2.852 |
| 45 | = 2.916 |
| 46 | = 2.980 |

| Grains. | Grams. |
|---|---|
| 47 | = 3.046 |
| 48 | = 3.110 |
| 49 | = 3.175 |
| 50 | = 3.240 |
| 51 | = 3.305 |
| 52 | = 3.370 |
| 53 | = 3.434 |
| 54 | = 3.499 |
| 55 | = 3.564 |
| 56 | = 3.629 |
| 57 | = 3.694 |
| 58 | = 3.758 |
| 59 | = 3.823 |
| 60 | = 3.888 |

| ℥ | Grams. |
|---|---|
| 1 | = 3.888 |
| 2 | = 7.776 |
| 3 | = 11.664 |
| 4 | = 15.552 |
| 5 | = 19.440 |
| 6 | = 23.328 |
| 7 | = 27.216 |
| 8 | = 31.103 |

| ℥ | Grams. |
|---|---|
| 1 | = 31.103 |
| 2 | = 62.207 |
| 3 | = 93.310 |
| 4 | = 124.414 |
| 5 | = 155.517 |
| 6 | = 186.621 |
| 7 | = 217.724 |
| 8 | = 248.823 |
| 9 | = 279.931 |
| 10 | = 311.035 |
| 11 | = 342.138 |
| 12 | = 373.250 |

| Lbs. | Kilos. |
|---|---|
| 1 | = 0.373 |
| 2 | = 0.747 |
| 3 | = 1.120 |
| 4 | = 1.493 |
| 5 | = 1.866 |
| 6 | = 2.240 |
| 7 | = 2.613 |
| 8 | = 2.986 |
| 9 | = 3.359 |
| 10 | = 3.733 |

1 pound Avdp. = 453.5925 gm.
1 kilo = 2.2046 lbs. Avdp.

## TABLE III.

### WEIGHT OF ONE CUBIC CENTIMETER OF NITROGEN.

| Temperatures in Centigrade. | 728 | 730 | 732 | 734 | 736 | 738 | 740 | 742 |
|---|---|---|---|---|---|---|---|---|
| 10° | 1.1466 | 1.1498 | 1.1529 | 1.1561 | 1.1593 | 1.1625 | 1.1657 | 1.1689 |
| 11° | 1.1415 | 1.1447 | 1.1479 | 1.1511 | 1.1542 | 1.1574 | 1.1606 | 1.1638 |
| 12° | 1.1364 | 1.1396 | 1.1428 | 1.1459 | 1.1491 | 1.1523 | 1.1554 | 1.1586 |
| 13° | 1.1314 | 1.1345 | 1.1377 | 1.1409 | 1.1440 | 1.1472 | 1.1503 | 1.1535 |
| 14° | 1.1263 | 1.1294 | 1.1326 | 1.1357 | 1.1389 | 1.1420 | 1.1452 | 1.1483 |
| 15° | 1.1211 | 1.1243 | 1.1274 | 1.1305 | 1.1337 | 1.1368 | 1.1399 | 1.1431 |
| 16° | 1.1160 | 1.1191 | 1.1222 | 1.1253 | 1.1285 | 1.1316 | 1.1347 | 1.1378 |
| 17° | 1.1107 | 1.1138 | 1.1170 | 1.1201 | 1.1232 | 1.1263 | 1.1294 | 1.1325 |
| 18° | 1.1054 | 1.1085 | 1.1117 | 1.1148 | 1.1179 | 1.1209 | 1.1241 | 1.1272 |
| 19° | 1.1001 | 1.1032 | 1.1063 | 1.1094 | 1.1125 | 1.1156 | 1.1187 | 1.1218 |
| 20° | 1.0948 | 1.0979 | 1.1009 | 1.1040 | 1.1071 | 1.1102 | 1.1133 | 1.1164 |
| 21° | 1.0894 | 1.0924 | 1.0955 | 1.0986 | 1.1017 | 1.1047 | 1.1078 | 1.1109 |
| 22° | 1.0839 | 1.0870 | 1.0900 | 1.0931 | 1.0961 | 1.0992 | 1.1023 | 1.1053 |
| 23° | 1.0784 | 1.0814 | 1.0845 | 1.0875 | 1.0906 | 1.0936 | 1.0967 | 1.0997 |
| 24° | 1.0728 | 1.0758 | 1.0789 | 1.0819 | 1.0849 | 1.0880 | 1.0910 | 1.0940 |
| 25° | 1.0671 | 1.0701 | 1.0732 | 1.0762 | 1.0792 | 1.0823 | 1.0853 | 1.0883 |
| | 728 | 730 | 732 | 734 | 736 | 738 | 740 | 742 |

| Temperatures in Centigrade. | 744 | 746 | 748 | 750 | 752 | 754 | 756 | 758 |
|---|---|---|---|---|---|---|---|---|
| 10° | 1.1721 | 1.1753 | 1.1785 | 1.1817 | 1.1848 | 1.1880 | 1.1912 | 1.1944 |
| 11° | 1.1670 | 1.1701 | 1.1733 | 1.1765 | 1.1717 | 1.1829 | 1.1860 | 1.1892 |
| 12° | 1.1618 | 1.1649 | 1.1681 | 1.1713 | 1.1744 | 1.1776 | 1.1808 | 1.1839 |
| 13° | 1.1566 | 1.1598 | 1.1630 | 1.1661 | 1.1693 | 1.1724 | 1.1756 | 1.1787 |
| 14° | 1.1515 | 1.1546 | 1.1577 | 1.1609 | 1.1640 | 1.1672 | 1.1703 | 1.1735 |
| 15° | 1.1462 | 1.1493 | 1.1525 | 1.1556 | 1.1587 | 1.1619 | 1.1650 | 1.1681 |
| 16° | 1.1409 | 1.1441 | 1.1472 | 1.1503 | 1.1534 | 1.1566 | 1.1597 | 1.1628 |
| 17° | 1.1356 | 1.1397 | 1.1419 | 1.1450 | 1.1481 | 1.1512 | 1.1543 | 1.1574 |
| 18° | 1.1303 | 1.1334 | 1.1365 | 1.1396 | 1.1427 | 1.1458 | 1.1489 | 1.1520 |
| 19° | 1.1248 | 1.1279 | 1.1310 | 1.1341 | 1.1372 | 1.1403 | 1.1434 | 1.1465 |
| 20° | 1.1194 | 1.1225 | 1.1256 | 1.1287 | 1.1318 | 1.1348 | 1.1379 | 1.1410 |
| 21° | 1.1139 | 1.1170 | 1.1201 | 1.1231 | 1.1262 | 1.1293 | 1.1324 | 1.1354 |
| 22° | 1.1084 | 1.1115 | 1.1145 | 1.1176 | 1.1206 | 1.1237 | 1.1268 | 1.1298 |
| 23° | 1.1028 | 1.1058 | 1.1089 | 1.1119 | 1.1150 | 1.1180 | 1.1211 | 1.1241 |
| 24° | 1.0971 | 1.1001 | 1.1032 | 1.1062 | 1.1092 | 1.1123 | 1.1153 | 1.1184 |
| 25° | 1.0913 | 1.0944 | 1.0974 | 1.1004 | 1.1035 | 1.1065 | 1.1095 | 1.1126 |
| | 744 | 746 | 748 | 750 | 752 | 754 | 756 | 758 |

Barometric pressure in millimeters.

TABLE III.—Continued.

WEIGHT OF ONE CUBIC CENTIMETER OF NITROGEN.

| Temperatures in Centigrade. | 760 | 762 | 764 | 766 | 768 | 770 | 772 | 774 |
|---|---|---|---|---|---|---|---|---|
| 10° | 1.1976 | 1.2008 | 1.2040 | 1.2072 | 1.2104 | 1.2136 | 1.2167 | 1.2199 |
| 11° | 1.1924 | 1.1956 | 1.1988 | 1.2019 | 1.2051 | 1.2083 | 1.2115 | 1.2147 |
| 12° | 1.1871 | 1.1903 | 1.1934 | 1.1966 | 1.1998 | 1.2029 | 1.2061 | 1.2093 |
| 13° | 1.1819 | 1.1851 | 1.1882 | 1.1914 | 1.1945 | 1.1977 | 1.2008 | 1.2040 |
| 14° | 1.1766 | 1.1798 | 1.1829 | 1.1861 | 1.1892 | 1.1923 | 1.1955 | 1.1986 |
| 15° | 1.1713 | 1.1744 | 1.1775 | 1.1807 | 1.1838 | 1.1869 | 1.1901 | 1.1932 |
| 16° | 1.1659 | 1.1691 | 1.1722 | 1.1753 | 1.1784 | 1.1816 | 1.1847 | 1.1878 |
| 17° | 1.1605 | 1.1636 | 1.1667 | 1.1699 | 1.1730 | 1.1761 | 1.1792 | 1.1823 |
| 18° | 1.1551 | 1.1582 | 1.1613 | 1.1644 | 1.1675 | 1.1706 | 1.1737 | 1.1768 |
| 19° | 1.1496 | 1.1527 | 1.1558 | 1.1589 | 1.1620 | 1.1650 | 1.1681 | 1.1712 |
| 20° | 1.1441 | 1.1472 | 1.1502 | 1.1533 | 1.1564 | 1.1595 | 1.1626 | 1.1657 |
| 21° | 1.1385 | 1.1416 | 1.1446 | 1.1477 | 1.1508 | 1.1539 | 1.1569 | 1.1600 |
| 22° | 1.1329 | 1.1359 | 1.1390 | 1.1421 | 1.1451 | 1.1482 | 1.1512 | 1.1543 |
| 23° | 1.1272 | 1.1302 | 1.1333 | 1.1363 | 1.1394 | 1.1424 | 1.1455 | 1.1485 |
| 24° | 1.1214 | 1.1244 | 1.1275 | 1.1305 | 1.1336 | 1.1366 | 1.1396 | 1.1427 |
| 25° | 1.1156 | 1.1186 | 1.1216 | 1.1247 | 1.1277 | 1.1307 | 1.1338 | 1.1368 |
| | 760 | 762 | 764 | 766 | 768 | 770 | 772 | 774 |

| Temperatures in Centigrade. | 776 | 778 | 780 | 782 | 784 | 786 | 788 | 790 |
|---|---|---|---|---|---|---|---|---|
| 10° | 1.2231 | 1.2263 | 1.2295 | 1.2327 | 1.2359 | 1.2391 | 1.2423 | 1.2454 |
| 11° | 1.2178 | 1.2210 | 1.2242 | 1.2274 | 1.2306 | 1.2337 | 1.2369 | 1.2401 |
| 12° | 1.2124 | 1.2156 | 1.2188 | 1.2219 | 1.2251 | 1.2283 | 1.2314 | 1.2346 |
| 13° | 1.2072 | 1.2103 | 1.2135 | 1.2166 | 1.2198 | 1.2229 | 1.2261 | 1.2293 |
| 14° | 1.2018 | 1.2049 | 1.2081 | 1.2112 | 1.2144 | 1.2175 | 1.2207 | 1.2238 |
| 15° | 1.1963 | 1.1995 | 1.2026 | 1.2057 | 1.2089 | 1.2120 | 1.2151 | 1.2183 |
| 16° | 1.1909 | 1.1942 | 1.1973 | 1.2004 | 1.2035 | 1.2067 | 1.2098 | 1.2129 |
| 17° | 1.1854 | 1.1885 | 1.1916 | 1.1947 | 1.1979 | 1.2010 | 1.2041 | 1.2072 |
| 18° | 1.1799 | 1.1831 | 1.1862 | 1.1893 | 1.1924 | 1.1955 | 1.1986 | 1.2017 |
| 19° | 1.1743 | 1.1774 | 1.1805 | 1.1836 | 1.1867 | 1.1898 | 1.1929 | 1.1960 |
| 20° | 1.1687 | 1.1718 | 1.1749 | 1.1780 | 1.1811 | 1.1841 | 1.1872 | 1.1903 |
| 21° | 1.1631 | 1.1661 | 1.1692 | 1.1723 | 1.1754 | 1.1784 | 1.1815 | 1.1846 |
| 22° | 1.1574 | 1.1604 | 1.1635 | 1.1665 | 1.1696 | 1.1727 | 1.1757 | 1.1788 |
| 23° | 1.1516 | 1.1546 | 1.1577 | 1.1607 | 1.1638 | 1.1668 | 1.1699 | 1.1729 |
| 24° | 1.1457 | 1.1488 | 1.1518 | 1.1548 | 1.1579 | 1.1610 | 1.1640 | 1.1671 |
| 25° | 1.1399 | 1.1429 | 1.1459 | 1.1489 | 1.1520 | 1.1550 | 1.1580 | 1.1610 |
| | 776 | 778 | 780 | 782 | 784 | 786 | 788 | 790 |

Barometric pressure in millimeters.

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